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CLAIMS

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(57) [Claim(s)]
[Claim 1] Composite for brazing and soldering equipped with Fe atom diffusion control layer which controls that Fe atom is spread in a wax material side from said base material in case laminating formation is carried out on the front face of the base material formed with iron steel materials, and said base material and the brazing and soldering of the joint material are carried out by Cu system wax material.
[Claim 2] Composite for brazing and soldering with which the clad of said base material and said Fe atom diffusion control layer was carried out by diffused junction and which was indicated in the 1st term of a claim.
[Claim 3] Composite for brazing and soldering equipped with Fe atom diffusion control layer which controls that Fe atom is spread in a wax material side from said base material in case laminating formation is carried out on the front face of the base material formed with iron steel materials, and said base material and the brazing and soldering of the joint material are carried out by Cu system wax material, and Cu system wax material layer by which laminating formation was carried out on said Fe atom diffusion control layer.
[Claim 4] Composite for brazing and soldering with which the clad of said base material, said Fe atom diffusion control layer, and said Cu system wax material layer of each other was carried out by diffused junction and which was indicated in the 3rd term of a claim.
[Claim 5] Composite for brazing and soldering which said base material was formed by stainless steel material, and was formed with nickel alloy with which said Fe atom diffusion control layer uses nickel or nickel as a principal component and which was indicated in any 1 term of the 1-4th terms of a claim.
[Claim 6] said base material forms by stainless steel material -- having -- said Fe atom diffusion control layer -- nickel or nickel -- more than 90wt% -- it contains and Remainder Cu is formed with the nickel-Cu alloy which becomes as an essential component -- having -- said Cu system wax material layer -- nickel -- 2 - 15wt% -- the composite for brazing and soldering which contained and indicated Remainder Cu in the 4th term of a claim formed with the Cu-nickel alloy which becomes as an essential component.
[Claim 7] the Cu-nickel alloy which forms said Cu system wax material layer -- nickel -- 5 - 10wt% -- the composite for brazing and soldering which contained and indicated Remainder Cu in the 6th term of a claim which becomes as an essential component.
[Claim 8] Composite for brazing and soldering whose thickness of said Fe atom diffusion control layer is 5 micrometers or more and which was indicated in any 1 term of the 1-7th terms of a claim.
[Claim 9] The base material in which was equipped with the part I material and the part II

material in which brazing and soldering were carried out to this part I material by Cu system wax material, and said part I material was formed with iron steel materials, The brazing-and-soldering structure which has Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from said base material in case a laminating is carried out to the front face of said base material and the brazing and soldering of said part I material and part II material are carried out.
[Claim 10] It is the brazing-and-soldering structure which said base material was formed with stainless steel, and was indicated in the 9th term of a claim in which said Fe atom diffusion control layer was formed with nickel alloy which uses nickel or nickel as a principal component.
[Claim 11] It has the plate member countered and arranged and the diaphragm which divides into much subspace sections the space section formed between said plate members. The plate-like base material in which the brazing and soldering of said plate member and said diaphragm were carried out by Cu system wax material, and said plate member was formed with stainless steel, The heat exchanger which has Fe atom diffusion control layer which consists of a nickel alloy which uses as a principal component nickel or nickel which controls that Fe atom is spread in the wax material section from said base material in case laminating formation is carried out and the brazing and soldering of said diaphragm and said plate member are carried out to the front face of said base material.
[Claim 12] The 1st crevice and the 1st heights counter the 1st concave heights material formed by turns and said 1st concave heights material, and are arranged. Have the 2nd concave heights material in which the 2nd crevice and the 2nd heights were formed by turns, and the brazing and soldering of the external surface of the 1st crevice of said 1st concave heights material and the external surface of the 2nd heights of said 2nd concave heights material are carried out by Cu system wax material. The base material in which said 1st concave heights material and the 2nd concave heights material were respectively formed with stainless steel, The heat exchanger which has Fe atom diffusion control layer which consists of a nickel alloy which uses as a principal component nickel or nickel which controls that Fe atom is spread in the wax material section from said base material in case laminating formation is carried out and the brazing and soldering of said 1st crevice and said 2nd heights are carried out to the front face of said base material.
[Claim 13] said Cu system wax material -- nickel -- 5 - 10wt% -- it contains and Remainder Cu is formed with the Cu-nickel alloy which becomes as an essential component -- having -- said Fe atom diffusion control layer -- nickel or nickel -- more than 90wt% -- the heat exchanger which contained and indicated Remainder Cu in the 11th term of a claim or the 12th term formed with the nickel-Cu alloy which becomes as an essential component.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
Technical field This invention relates to the composite for brazing and soldering used as the brazing-and-soldering structures, such as heat exchangers, such as a radiator and a gas cooler, and a material of those.
Background technique The interest about an environmental problem is increasing internationally in recent years, and exhaust gas reduction of an automobile is strongly required increasingly as part of that. Various kinds of purges, such as a thermal reactor which is made to already afterburn exhaust gas and sets CO and HC to CO2 and H2O as a cure against exhaust gas purification of an automobile, and a catalytic converter, are put in practical use.
Conventionally, in an exhaust gas purge etc., the heat exchanger used in a hot corrosive gas ambient atmosphere is formed with the stainless steel excellent in corrosion resistance, and the brazing and soldering of each part material of a heat exchanger are further carried out nickel:1-5% by a corrosion resistance good copper wax with the melting point of 1000 degrees C or more, Mn;5-20% indicated by JP,60-72695,A, or CU system wax material which becomes a remainder real target from Cu.
Since the corrosive environment in a heat exchanger is becoming severe much more by change of an exhaust gas presentation etc. and problems, such as corrosion by the condensate of exhaust gas, are also produced recently, much more improvement is called for from the corrosion resistance of wax material. The demand to the corrosion resistance of the wax material put to such high corrosive environment is just going to be called for also in exhaust gas heat exchangers, such as a gas turbine engine instead of the problem of only the emission-gas-purification system of an automobile, and the various brazing-and-soldering iron structural steelworks put to high corrosive environment.
However, the present condition is that the wax material which satisfies such a corrosion resistance demand enough is not yet supplied to a commercial scene. When nickel wax with which corrosion resistance is said to be good is used, under the environment where exhaust gas dews in hot environments although it is satisfactory, corrosion advances too. Although this reason is not necessarily clear, it is also surmised that it is one of the causes that melting point fall elements, such as B and Si, are added by nickel wax. Moreover, even if it uses the Cu-nickel alloy wax material which added comparatively many nickel which is a corrosion-resistant improvement element, sufficient corrosion resistance is not acquired. And the phenomenon in which corrosion resistance deteriorated was also accepted, so that there were many amounts of nickel.
This invention aims at offering the brazing-and-soldering structures, such as a heat exchanger excellent in the corrosion resistance in the charge of brazing-and-soldering material which can raise the corrosion resistance of the wax material section, and the wax material section put to a corrosion ambient atmosphere, in the brazing-and-soldering structure with which the brazing and soldering of the member formed with the various iron steel materials which were made in view of this technical problem, and contain stainless steel material were carried out. This purpose is attained by the following invention.
Indication of invention In case laminating formation is carried out on the front face of the base material formed with iron steel materials, and said base material and the charge of brazing-and-soldering material of this invention carries out the brazing and soldering of the joint material by Cu system wax material, it is the composite for brazing and soldering equipped with Fe atom

diffusion control layer which controls that Fe atom is spread in a wax material side from said base material.
Since Fe atom diffusion control layer is formed on the surface of the base material according to this invention, in order to spread Fe atom in a base material in a wax material side in the case of brazing and soldering, it is necessary to carry out spreading diffusion of the Fe atom diffusion control layer first. Since diffusion of Fe atom in Fe atom diffusion control layer turns into solid phase diffusion, the diffusion rate of Fe atom becomes remarkably slow as compared with diffusing the inside of the wax material of a melting condition. For this reason, Fe atom can prevent being spread in wax material only by preparing very thin Fe atom diffusion control layer. Consequently, the wax material section of the brazing-and-soldering structure can demonstrate now the corrosion resistance which Cu system wax material originally has, and its corrosion resistance improves.
In this invention, Cu system wax material layer can be formed on Fe atom diffusion control layer. Moreover, the clad of Fe atom diffusion control layer and the Cu system wax material layer can be carried out for a base material and Fe atom diffusion control layer by diffused junction again. moreover, as it was alike and being indicated, said base material can be formed with nickel alloy which uses nickel or nickel as a principal component for said Fe atom diffusion control layer by stainless steel material. When carrying out the clad of a base material, Fe atom diffusion control layer, and the Cu system wax material layer by diffused junction, a base material moreover, by stainless steel material Fe atom diffusion control layer -- nickel or nickel -- more than 90wt% -- it containing and Remainder Cu with the nickel-Cu alloy which becomes as an essential component said Cu system wax material layer -- nickel -- 2 - 15wt% -- more -- desirable -- 5 - 10wt% -- it is good to contain and to form Remainder Cu with the Cu-nickel alloy which becomes as an essential component. Furthermore, the thickness of said Fe atom diffusion control layer is good to be referred to as 5 micrometers or more.
Moreover, the brazing-and-soldering structure of this invention is equipped with the part I material and the part II material in which brazing and soldering were carried out to this part I material by Cu system wax material. Said part I material has Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from said base material, in case a laminating is carried out to the front face of the base material formed with iron steel materials, and said base material and the brazing and soldering of said part I material and part II material are carried out.
According to this invention, in order that Fe atom in the base material of the part I material may carry out solid phase diffusion of the Fe atom diffusion control layer first in the case of brazing and soldering, carrying out diffusion invasion at the wax material side of a melting condition is controlled. For this reason, Fe atom can prevent being spread in wax material only by preparing very thin Fe atom diffusion control layer. Consequently, the wax material section of the brazing-and-soldering structure can demonstrate now the corrosion resistance which Cu system wax material originally has, and its corrosion resistance improves. When the part II material has the base material formed with iron steel materials, it is desirable like the part I material to form Fe atom diffusion control layer on a base material. By this, it can also be controlled that Fe atom is spread from the base material of the part II material to the wax material section, and the corrosion resistance of the wax material section can be raised more.
In said brazing-and-soldering structure, said base material can be formed with stainless steel, and said Fe atom diffusion control layer can be formed with nickel alloy which uses nickel or nickel as a principal component. In this case, in order the base material itself is excellent in corrosion

resistance and for the coefficient of thermal expansion of Fe atom diffusion control layer and a base material to approximate further, in the joint of Fe atom diffusion control layer and a base material, generating of thermal stress is controlled under wide range temperature, and the endurance of a joint can be raised.

Moreover, the heat exchanger of this invention is equipped with the plate member arranged face to face and the diaphragm which divides into much subspace sections the space section formed between said plate members. The brazing and soldering of said plate member and said diaphragm are carried out by Cu system wax material. It has Fe atom diffusion control layer which consists of a nickel alloy which uses as a principal component nickel or nickel which controls that Fe atom diffuses said plate member in the wax material section from said base material in case laminating formation is carried out and the brazing and soldering of said diaphragm and said plate member are carried out to the front face of the plate-like base material formed with stainless steel, and said base material.

According to this invention, in order that Fe atom in the base material of a plate member may carry out solid phase diffusion of the Fe atom diffusion control layer first in the case of brazing and soldering, very thin Fe atom diffusion control layer is only prepared, and carrying out diffusion invasion at the wax material side of a melting condition is prevented. Consequently, the wax material section of the heat exchanger which is the brazing-and-soldering structure can demonstrate the corrosion resistance which wax material originally has, and its corrosion resistance improves. Moreover, the base material itself is excellent in corrosion resistance, further, since Fe atom diffusion control layer is formed with nickel alloy which uses nickel or nickel as a principal component and the stainless steel and coefficient of thermal expansion of a base material approximate it, generating of thermal stress is controlled under wide range temperature, and it can raise the endurance of a heat exchanger.

Moreover, the heat exchanger of this invention is equipped with the 1st concave heights material in which the 1st crevice and the 1st heights were formed by turns, and the 2nd concave heights material in which said 1st concave heights material was countered, it has been arranged, and the 2nd crevice and the 2nd heights were formed by turns. The brazing and soldering of the external surface of the 1st crevice of said 1st concave heights material and the external surface of the 2nd heights of said 2nd concave heights material are carried out by Cu system wax material. Said 1st concave heights material and the 2nd concave heights material have Fe atom diffusion control layer which consists of a nickel alloy which uses as a principal component nickel or nickel which controls that Fe atom is spread in the wax material section from said base material, in case laminating formation is carried out and the brazing and soldering of said 1st crevice and said 2nd heights are carried out to the front face of the base material respectively formed with stainless steel, and said base material.

According to this invention, in order that Fe atom in each base material of the 1st concave heights material and the 2nd concave heights material may carry out solid phase diffusion of the Fe atom diffusion control layer of each part material first in the case of brazing and soldering, very thin Fe atom diffusion control layer is only prepared on each base material, and carrying out diffusion invasion at the wax material side of a melting condition is prevented. Consequently, the wax material section of the heat exchanger which is the brazing-and-soldering structure can demonstrate the corrosion resistance which wax material originally has, and its corrosion resistance improves. Moreover, the base material itself is excellent in corrosion resistance, further, since Fe atom diffusion control layer is formed with nickel alloy which uses nickel or nickel as a principal component and the stainless steel and coefficient of thermal expansion of a

base material approximate it, generating of thermal stress is controlled under wide range temperature, and it can raise the endurance of a heat exchanger.
said heat exchanger -- setting -- said Cu system wax material -- nickel -- 5 - 10wt% -- the Cu-nickel alloy which contains and becomes considering Remainder Cu as an essential component -- said Fe atom diffusion control layer -- nickel or nickel -- more than 90wt% -- it can contain and the corrosion resistance of the wax material section can be further raised by forming Remainder Cu with the nickel-Cu alloy which becomes as an essential component.
Easy explanation of a drawing Drawing 1 is the fragmentary sectional view of the composite for brazing and soldering concerning the operation gestalt of this invention.
Drawing 2 is 10min at 1100 degrees C about the composite for brazing and soldering which formed Cu system wax material layer by pure Cu. It is the distribution map of nickel concentration in the wax material layer front face from the base material interface at the time of holding, and Fe concentration.
Drawing 3 is 10min at 1150 degrees C about the composite for brazing and soldering which formed Cu system wax material layer with the Cu-2wt%nickel alloy. It is the distribution map of nickel concentration in the wax material layer front face from the base material interface at the time of holding, and Fe concentration.
Drawing 4 is 10min at 1150 degrees C about the composite for brazing and soldering which formed Cu system wax material layer with the Cu-5wt%nickel alloy. It is the distribution map of nickel concentration in the wax material layer front face from the base material interface at the time of holding, and Fe concentration.
Drawing 5 is 10min at 1150 degrees C about the composite for brazing and soldering which formed Cu system wax material layer with the Cu-10wt%nickel alloy. It is the distribution map of nickel concentration in the wax material layer front face from the base material interface at the time of holding, and Fe concentration.
Drawing 6 is 10min at 1200 degrees C about the composite for brazing and soldering which formed Cu system wax material layer with the Cu-20wt%nickel alloy. It is the distribution map of nickel concentration in the wax material layer front face from the base material interface at the time of holding, and Fe concentration.
Drawing 7 is drawing showing the relation of the nickel content and the rate of corrosion weight loss in Cu-nickel alloy wax material.
Drawing 8 is 10min at 1100 degrees C about the brazing-and-soldering composite concerning an example. It is Fe concentration distribution map of the direction of board thickness of the base material interface at the time of holding to Fe atom diffusion control layer.
Drawing 9 is 10min at 1050 degrees C about the brazing-and-soldering composite concerning an example. It is Fe concentration distribution map of the direction of board thickness of the base material interface at the time of holding to Fe atom diffusion control layer.
Drawing 10 is 10min at 1000 degrees C about the brazing-and-soldering composite concerning an example. It is Fe concentration distribution map of the direction of board thickness of the base material interface at the time of holding to Fe atom diffusion control layer.
Drawing 11 is 10min at 1100 degrees C about the brazing-and-soldering composite concerning the example of a comparison in which Fe atom diffusion control layer is not formed. It is Fe concentration distribution map of the direction of board thickness of the base material interface at the time of holding to a wax material layer.
Drawing 12 is the partial perspective view of the heat exchanger concerning the 1st operation gestalt.

Drawing 13 is the fragmentary sectional view of the heat exchanger concerning the 2nd operation gestalt.
Drawing 14 is the fragmentary sectional view and partial expanded sectional view of the compound member for concave convex brazing and soldering which were used for manufacture of the heat exchanger of the 2nd operation gestalt.
Drawing 15 is the state diagram of a Cu-nickel binary system alloy.
The best gestalt for inventing this invention person studied the cause by which the corrosion resistance of the wax material section deteriorated, in the brazing-and-soldering structure which carried out the brazing and soldering of the joint material formed with iron steel materials, such as stainless steel, by Cu system wax material. Consequently, if brazing and soldering were carried out at an elevated temperature which exceeds 900 degrees C, since diffusion invasion would be carried out into the wax material which Fe atom fused from iron steel materials and Fe atom would be spread even on the front face of the wax material section, the original corrosion resistance of Cu system wax material before the corrosion resistance of the wax material section joining could not be demonstrated, but the knowledge of deteriorating was carried out. That is, since Fe is easy to be corroded from Cu and Fe and Cu constitute a local battery, the corrosion resistance in the wax material section comes to deteriorate as compared with the corrosion resistance which Cu system wax material used on the occasion of brazing and soldering originally has. For this reason, if the wax material section after the brazing and soldering in which Fe carried out diffusion invasion is put to a corrosion ambient atmosphere, it will become that it is easy to be corroded. In addition, although nickel and Cr in the alloy element in iron steel materials, for example, stainless steel, are also diffused in a wax material side in the case of brazing and soldering, since nickel dissolves to Cu, corrosion resistance is not spoiled, and since the diffusion rate is slow, Cr is considered not to be spread to the forge fire which spoils corrosion resistance as compared with Fe. This invention is completed by this knowledge.
Hereafter, this invention is explained to a detail based on an operation gestalt.
Drawing 1 shows the composite 1 for brazing and soldering concerning the operation gestalt of this invention, laminating formation of the Fe atom diffusion control layers 12 and 12 is carried out to both sides of the plate-like base material 11, and laminating formation of the Cu system wax material layers 13 and 13 is carried out on it.
If it is the iron steel materials which use Fe as a principal component as said base material 11, anything of the quality of the material is applicable. It is good to form suitably, corrosion resistance good iron steel materials, for example, stainless steel material etc., etc.
It can form with the metal which the melting point is higher than wax material, and dissolves with Cu as said Fe atom diffusion control layer 12 excluding Fe, therefore the metal which does not generate the sludge which is easy to become the origin of corrosion. for example, -- pure -- nickel alloy which uses nickel and nickel as a principal component (preferably 50wt(s)% more than), Cr, Mo, W, Nb, Ti, etc. can be used. As said nickel alloy, a nickel-Cu alloy, a nickel-Cr alloy, and a nickel-Mo alloy can be illustrated. When plastic workability is taken into consideration, it is desirable to carry out to more than nickel>=90wt% with a nickel-Mo system alloy nickel>=70wt% with said nickel-Cr system alloy. Moreover, as a nickel alloy, the fundamental property of an alloy besides said alloy elements, such as Cr and Mo, may not be spoiled, but mechanical and the thing contained auxiliary are sufficient as the element which raises chemical property. In addition, although it is difficult to carry out the pressure welding of this to a base material by the clad method when Fe atom diffusion control layer is formed with refractory metals, such as W and Mo, laminating formation can be carried out on the surface of a

base material by thermal spraying, and PVD and CVD.
When said base material 11 is formed with stainless steel, as for Fe atom diffusion control layer 12, it is desirable to form with said pure nickel or nickel alloy (for both to be collectively called nickel basic metal). Since the coefficient of thermal expansion of stainless steel and nickel is close, by forming Fe atom diffusion control layer 12 by nickel basic metal, in the joint of Fe atom diffusion control layer 12 and a base material 11, generating of thermal stress can be controlled under wide range temperature, and the endurance of a joint can be raised. Incidentally, Cr system stainless steel whose nickel-Cr system stainless steel whose coefficient of thermal expansion in 30-600 degrees C is SUS304 of JIS is 18.3x10-6 /430 is 11.8x10-6/K, to nickel being 15.4x10-5/K, Mo stops at K and 5.7x10-6/W stops at 4.6x10-6/K. [K and SUS430] In addition, the use upper limit temperature of the heat exchanger for exhaust gas is usually about 600 degrees C.
pure as said Cu system wax material layer 13 -- a Cu-nickel alloy, Cu alloy for various kinds of well-known others and wax material, for example, a Cu-Mn alloy, and a Cu-Mn-nickel alloy can be used. [Cu] the alloy element which adds Cu content to Cu -- beyond about 10wt% -- what is necessary is just to be In addition, although what is necessary is just to make temperature of brazing and soldering into the temperature of under the melting point of the metal which forms Fe atom diffusion control layer above the melting point of Cu system wax material, it is usually made into temperature with a melting point [of Cu system wax material] of about +20 degrees C. By using Cu system wax material whose melting point is about 880-1180 degrees C, brazing-and-soldering temperature can be made into about 900-1200 degrees C, and annealing and brazing and soldering of iron steel materials which contain stainless steel with heating for [several minute - number] 10 minutes can be performed to coincidence.
In this composite 1 for brazing and soldering, since laminating formation of the Cu system wax material layer 13 is carried out on Fe atom diffusion control layer 12, in case brazing work is performed, the complicated activity of attaching the wax material prepared separately between the joint material which is the objects of brazing and soldering can become unnecessary, it can excel in brazing work nature, and productivity can be raised.
Various approaches, such as plating besides the clad by diffused junction, thermal spraying, and PVD, CVD, are applicable to laminating formation of Fe atom diffusion control layer 12 to said base material 11. But without generating the pinhole which poses a problem in plating, if the clad of a base material 11 and the Fe atom diffusion control layer 12 is carried out by diffused junction, after pressing down each material, by carrying out homogenizing, both can be unified easily and it excels in industrial productivity. Moreover, the thickness of Fe atom diffusion control layer 12 is also easily controllable only by adjusting the rolling reduction in the case of a draft. Moreover, when forming Cu system wax material layer 13 on Fe atom diffusion control layer 12, the clad of adjoining each part can be easily carried out by making each material of a base material 11, Fe atom diffusion control layer 12, and Cu system wax material layer 13 pile up mutually respectively, pressing it down, and carrying out homogenizing.
the case where the clad of said base material 11, Fe atom diffusion control layer 12, and the Cu system wax material layer 13 is carried out -- Fe atom diffusion control layer 12 -- pure nickel or nickel -- more than 90wt% -- it is desirable to contain, to form Remainder Cu with the nickel-Cu alloy which becomes as an essential component, and to, form Cu system wax material layer on the other hand with the Cu-nickel alloy which becomes considering Remainder Cu as an essential component 2 - 15wt% about nickel. When nickel carries out the clad of high-concentration Fe atom diffusion control layer 12 beyond 90wt%, and the Cu system wax material

layer 13 of the high concentration [Cu] of 98wt% **, a guide is generated near a junction interface according to the car KENDORU effectiveness, and there is a possibility that the dimension system of the composite for brazing and soldering may be spoiled. Moreover, if the amount of nickel of Cu system wax material layer 13 exceeds 15wt(s)%, the melting point of wax material will come to exceed 1200 degrees C, and whenever [stoving temperature / in the case of brazing and soldering] will become high too much.
Furthermore, when pure nickel or nickel forms Fe atom diffusion control layer 12 with the nickel-Cu alloy beyond 90wt%, as for Cu system wax material layer, it is more desirable to form nickel 5 - 10wt% with the Cu-nickel alloy which becomes considering Remainder Cu as an essential component. making the amount of nickel of Cu system wax material layer more than 5wt% -- the car KENDORU effectiveness -- it can prevent -- further -- the melting point of wax material -- 1100 degrees C -- super- -- ** -- a sake -- the clad back -- pure in the annealing temperature of the composite for brazing and soldering -- it can raise more than it near the melting point (1083 degrees C) of Cu. By raising annealing temperature, even when the iron steel materials which contain stainless steel as a base material 11 are used, a base material can fully be softened, and the moldability of the composite for brazing and soldering and workability can be raised now. On the other hand, by considering as less than [10wt%], the melting point of wax material becomes about 1180 degrees C or less, and brazing and soldering with a temperature of about 1200 degrees C or less become possible. Moreover, by making nickel of a Cu-nickel alloy into 5 - 10wt%, in case the brazing and soldering of the joint material are carried out, nickel is moderately spread into the wax material which is in a melting condition from Fe atom diffusion control layer 12 containing high-concentration nickel, and the amount of nickel of the wax material section after brazing and soldering becomes about 15-25wt%. Since the wax material section which consists of this Cu-nickel alloy is excellent in corrosion resistance, it can demonstrate the corrosion resistance which was excellent also to the exhaust gas condensate.
In order to confirm the corrosion-resistant improvement effectiveness at the time of forming said Cu system wax material layer with the Cu-nickel alloy which becomes considering Remainder Cu as an essential component 5 - 10wt% about nickel, corrosion-resistant investigation was conducted using the composite for brazing and soldering concerning the following examples 1-5.
The composite for brazing and soldering of the example 1 used for investigation To stainless steel sheet steel (base material material) with a thickness of 2000 micrometers formed with the SUS304 stainless steel of JIS, nickel foil with a thickness of 100 micrometers (Fe atom diffusion control layer material), Furthermore, the laminating of the pure Cu foil was carried out as a Cu system wax foil (Cu system wax layer material) with a thickness of 50 micrometers, roll pressing down was carried out at 60% of rolling reduction, the pressure welding of each part was carried out, and homogenizing for 1050 degree-Cx 3 minutes was given, and further, at 50% of rolling reduction, roll pressing down was carried out and it was manufactured. Only the quality of the materials of Cu system wax foil differ to the manufacture conditions of an example 1, and with an example 1, examples 2-5 summarize the quality of the material of Cu system wax material foil of examples 2-5 below, and are shown. The whole thickness of the composite of each manufactured example was 430 micrometers, and the base material was [20 micrometers and Cu system wax material layer of 400 micrometers and Fe atom diffusion control layer (nickel layer)] 10 micrometers. When appearance observation of the manufactured composite for brazing and soldering was carried out, the bulge section with the example 1 local on a front face which formed Cu system wax material layer by pure Cu was observed in some places.
example 1: -- pure -- Cu example 2:Cu-2wt%nickel alloy example 3:Cu-5wt%nickel alloy

example 4:Cu-10wt%nickel alloy example 5:Cu-20wt%nickel alloy The composite for brazing and soldering concerning five kinds of examples manufactured as mentioned above It is heated with a vacuum heating furnace on the heating conditions (whenever [stoving temperature] x holding time) shown in following investigation No.1-5. After being cooled radiationally to the room temperature, the amount of nickel and the amount of Fe(s) like each part in the thickness direction of Fe atom diffusion control layer and the wax material layer after coagulation were measured by EPMA (electron probe microanalyser) from the interface of a base material. The result is shown in drawing 2 -6. L12 and L13 in drawing mean Fe atom diffusion control layer after heating cooling, and a wax material layer. The written contents in following investigation No. are indicated in order of the class of used composite for brazing and soldering, heating conditions, and a measurement result.

(1) Investigation No.1 : 1 or 1100 degrees-C x10min of examples, and drawing 2 (2) Investigation No.2 : [2 or 1150 degrees-C x10min of examples,] Drawing 3 (3) Investigation No.3 : [3 or 1150 degrees-C x10min of examples,] Drawing 4 (4) Investigation No.4 : [4 or 1150 degrees-C x10min of examples,] Drawing 5 (5) Investigation No.5: 5 or 1200 degrees-C x10min of examples, drawing 6 In drawing 2 which shows the case where Cu system wax material layer is formed by pure Cu, it turns out that the amount of nickel has become or less about 5wt% from the front face of the wax material layer L13 after heating in the about 5-micrometer surface section. Moreover, by drawing 3 which shows the case where Cu system wax material layer is formed with a Cu-2wt%nickel alloy, about 10wt% contains the amount of nickel in the wax material layer L13. In drawing 4 which shows the case where this layer is formed with a Cu-5wt%nickel alloy, about 15wt% contains at least. At drawing 5 which shows the case where this layer is formed with a Cu-10wt%nickel alloy, it turns out that about 30wt% contains by drawing 6 which shows the case where about 20wt% contained and this layer is formed with a Cu-20wt%nickel alloy. On the other hand, although whenever [stoving temperature] was an elevated temperature comparatively as for the amount of Fe(s), in any case, in Fe atom diffusion control layer L12, it became about 0% from the base material interface by about 10 micrometers, and Fe atom was not accepted in the wax material layer L13.

Next, in order to investigate the corrosion resistance of the wax material layer in the example composite after heating, the wax material of pure Cu, a Cu-10wt%nickel alloy, a Cu-20wt%nickel alloy, and a Cu-30wt%nickel alloy was prepared, and the corrosion test investigated the corrosion resistance. Although the corrosive environment by exhaust gas needed to take into consideration the dew-point-corrosion environment which mainly poses a problem at the time of an engine shutdown, and the high-temperature-corrosion environment which mainly poses a problem at the time of engine operation, since especially the former corrosion resistance was a problem, the corrosion test was performed under the conditions over said dew-point-corrosion environment. Said corrosion test prepared the simulation water of condensation of the following presentation which simulated the exhaust gas condensate, carried out 500hr immersion of each above-mentioned wax material into the 100-degree C simulation water of condensation, and was carried out by measuring the mass (corrosion weight loss) of the wax material which decreased by immersion.

- Simulation water-of-condensation presentation (pH4.4)

Cl-: 20ppm, SO42-:350ppm, NO3-:150ppm, NH4+:700ppm, formic-acid:500ppm, an acetic acid: 700 ppm A corrosion test result is shown in drawing 7 . The axis of ordinate in drawing shows the rate of corrosion weight loss which **(ed) corrosion weight loss with the mass of the wax material before being immersed. Drawing 7 shows that corrosion resistance is best, when

nickel content is about 15-25wt%. Having the corrosion resistance the example 3 which used the Cu-5wt%Cu alloy, and especially the example 4 using a Cu-10wt%nickel alloy excelled [corrosion resistance] this in the composite for brazing and soldering of said example as a Cu system wax material layer is understood.

Next, the thickness of said Fe atom diffusion control layer 12 in the brazing-and-soldering composite 1 is explained to a detail.

When carrying out the brazing and soldering of the stainless steel members, it is good to set brazing-and-soldering temperature as about 1000-1200 degrees C so that annealing of a stainless steel member can also be performed in the case of brazing and soldering. By setting preferably 5 micrometers or more of thickness of Fe atom diffusion control layer 12 to 8 micrometers or more, extent inhibition can be carried out and, also in the case of brazing and soldering in this elevated temperature, what Fe atom from a base material 11 does for diffusion invasion at a wax material side can raise the remarkable corrosion resistance which is the wax material section. By being more preferably referred to as 10 micrometers or more, the diffusion by the side of the wax material of Fe atom can be prevented almost certainly also in an about 1200-degree C elevated temperature a passage clear from drawing 2 -6. Of course, as well as the case where a base material is formed by stainless steel material when a base material forms with iron steel materials other than stainless steel, annealing of a base material and the diffusion depressor effect of Fe atom can be acquired by 1000-1200-degree C brazing and soldering by setting more preferably 5 micrometers or more of 8 micrometers or more of thickness of Fe atom diffusion control layer to 10 micrometers or more.

Here, the relation between the thickness of Fe atom diffusion control layer and Fe atom diffusion depressor effect is concretely explained based on the heat test which simulated brazing and soldering.

The composite for brazing and soldering of an example used for the heat test To stainless steel sheet steel (base material blank) with a thickness of 1050 micrometers formed with the SUS304 stainless steel of JIS, nickel foil with a thickness of 200 micrometers (Fe atom diffusion control layer material), The laminating of the Cu system wax foil (Cu system wax layer material) which furthermore consists of a 15%Mn-10%nickel-Cu alloy with a thickness of 250 micrometers was carried out, roll pressing down was carried out at 60% of rolling reduction, the pressure welding of each part was carried out, and homogenizing for 800 degree-Cx 10 minutes was given, and further, at 30% of rolling reduction, roll pressing down was carried out and it was manufactured. Thus, the whole thickness of the manufactured composite was 420 micrometers, and the base material was [50 micrometers and Cu system wax material layer of 300 micrometers and Fe atom diffusion control layer (nickel layer)] 70 micrometers. On the other hand, the composite for brazing and soldering which carried out laminating formation of the direct Cu system wax material layer was prepared for the base material as an example of a comparison, without forming Fe atom diffusion control layer 12. The quality of the material of the base material of said example of a comparison and thickness were the same as that of an example, and Cu system wax material used the Cu-36wt%Mn-36.5wt%nickel alloy, and set the thickness to the same 70 micrometers as an example.

After the composite for brazing and soldering of an example and the example of a comparison was heated with the vacuum heating furnace on the heating conditions (whenever [stoving temperature] x holding time) shown in following investigation No.11-14 and being cooled radiationally to the room temperature, the amount of Fe(s) like each part in the thickness direction of Fe atom diffusion control layer (in the case of an example) or a wax material layer

(in the case of the example of a comparison) was measured by EPMA from the interface of a base material. The result is shown in drawing 8 -11. The written contents in following investigation No. are indicated in order of the class of used composite, heating conditions, and a measurement result.
(1) Investigation No.11 : an example, 1100 degree-Cx10min, and drawing 8 (2) Investigation No.12 : [Example,] 1050 degree-Cx10min and drawing 9 (3) Investigation No.13 : [Example,] 1000 degree-Cx10min and drawing 10 (4) Investigation No.14: The example of a comparison, 1100 degree-Cx10min, drawing 11 From drawing 11 , in the example of a comparison, Fe concentration gradually decreased from 42wt(s)% to 6wt(s)% from a base material interface to 9 micrometers, and this concentration was shown to the front face of a wax material layer after that. On the other hand, in the example, although Fe concentration was 42 - 44% in the base material interface, Fe concentration became 0% from the interface in nickel layer by 6 micrometers (in the case of drawing 9 and drawing 10), or 8 micrometers (in the case of drawing 8). This shows that Fe atoms which carry out diffusion invasion decrease in number sharply at a wax material layer only by forming about 5 micrometers of Fe atom diffusion control layers 12. Moreover, it turns out by carrying out 8-micrometer or more laminating formation of the Fe atom diffusion control layer 13 that whenever [stoving temperature] can prevent diffusion invasion of Fe atom from a base material to Cu system wax material layer below about 1100 degrees C. Therefore, in the composite 1 for brazing and soldering of an operation gestalt, and the brazing-and-soldering structure assembled by brazing and soldering using this, it turns out that the diffusion invasion by the side of the wax material of Fe atom in a base material 11 can be decreased sharply, and the original corrosion resistance of Cu system wax material is demonstrated only by carrying out laminating formation of the very thin Fe atom diffusion control layer 12 on a base material 11.
As mentioned above, although the operation gestalt explained the composite for brazing and soldering of this invention, this invention is not restrictively interpreted by this.
For example, with the above-mentioned operation gestalt, although laminating formation of Fe atom diffusion control layer 12 and the Cu system wax material layer 13 was carried out at the both sides of a base material 11, joint material may carry out the laminating of these only to the one side side of the base material by which brazing and soldering are carried out.
Moreover, although the clad of the Cu system wax material layer 13 besides Fe atom diffusion control layer 12 was carried out, Cu system wax material layer 13 is not necessarily required of the above-mentioned operation gestalt. In this case, Cu system wax material prepared separately is attached between the composite for brazing and soldering, and joint material, and should just carry out brazing and soldering.
Next, the operation gestalt of the brazing-and-soldering structure using the composite 1 for brazing and soldering concerning the above-mentioned operation gestalt as a material is explained.
Drawing 12 is the perspective view showing the passage structure of the heat exchanger concerning the 1st operation gestalt. In 2 sets of plate members which the plate member 21-1 of the lot countered and arranged and 21-2 separate predetermined spacing, are arranged at two or more set parallel, and adjoin mutually The diaphragm of the shape of bellows by which crookedness formation of the cross section was carried out in the example of drawing at the wave between the plate member 21-2 of the top group bottom, and the plate member 21-1 of the bottom group top which countered this plate member 21-2, and has been arranged (it is also called a fin.) 22 is interposed. Let the plate member 21-1 of said lot, and the space section between 21-2 be the medium passage where heat exchange media, such as cooling water, flow.

On the other hand, let the subspace section of a large number divided by said diaphragm 22 be the gas passageway to which high-temperature-corrosion nature gas, such as exhaust gas, flows between the plate member 22-2 of the top group bottom, and the plate member 21-1 of a bottom group top. In addition, the plate member 21-1 of a lot and 21-2 may be explained, using 21 as a sign of a plate member, when not distinguishing both.
As for each diaphragm 22, the brazing and soldering of the top face of the lower plate member 21-1 where the topmost part of wave heights and the inferior surface of tongue of the plate member 21-2 of the bottom which pinches this diaphragm 22 pinch the bottom and the diaphragm 22 of a wave crevice by brazing and soldering being carried out by Cu system wax material are similarly carried out by Cu system wax material.
Compound member 21A for plate-like brazing and soldering which processed into proper magnitude the composite 1 for brazing and soldering which has the structure shown in drawing 1 is used for the material of the plate member 21 of said heat exchanger. Expedient top [of explanation] and compound member 21for this plate-like brazing and soldering A is also explained with reference to drawing 1 . The clad of Fe atom diffusion control layer 12 which becomes both sides of the base material 11 of the shape of sheet metal formed with the austenitic stainless steel (SUS304 stainless steel of JIS) which was able to choose compound member 21A for plate-like brazing and soldering for anticorrosion acid resistance from nickel layer, and the Cu system wax material layer 13 which consists of a Cu-15wt%Mn-10wt%nickel alloy or a Cu-8wt%nickel alloy on it is carried out by diffused junction. On the other hand, said diaphragm 22 processes into a wave the sheet metal which consists of said stainless steel.
for assembling a heat exchanger using said compound member 21for plate-like brazing and soldering A and diaphragm 22 -- a diaphragm 22 and compound member 21A for plate-like brazing and soldering -- alternation -- piling up -- drawing 12 -- like -- a laminating -- carrying out -- shape retention -- carrying out -- the inside of a vacuum or a reducing gas ambient atmosphere -- under the melting point of Fe atom diffusion control layer 12 -- the temperature more than the melting point of Cu system wax material layer 13 -- it heats for the number 10 minutes of several minute - at 1100-1200 degrees C preferably. Cu system wax material layer 13 of compound member 21A for plate-like brazing and soldering fuses, and the brazing and soldering of the diaphragm 22 are carried out to a base material 11 through Fe atom diffusion control layer 12 by this.
Corrosive degradation to which it originated in diffusion of Fe atom since carrying out diffusion mixing into Cu system wax material which Fe atom fused from the base material 11 on the occasion of brazing and soldering was controlled by Fe atom diffusion control layer 12 is prevented, and the wax material section which Cu system wax material layer 13 once fused, and solidified on the occasion of brazing and soldering is excellent in corrosion resistance. Especially when Cu system wax material layer 13 is formed with said Cu-nickel alloy, in order that nickel of optimum dose may carry out diffusion mixing in the wax material section from nickel layer in the case of brazing and soldering, the corrosion resistance of the wax material section becomes what was very excellent.
Said compound member 21A for plate-like brazing and soldering actually used for manufacture of a heat exchanger To stainless steel sheet steel (base material blank) with a thickness of 1050 micrometers, nickel foil with a thickness of 200 micrometers (Fe atom diffusion control layer material), The laminating of the Cu system wax foil (Cu system wax layer material) which furthermore consists of a Cu-Mn-nickel alloy with a thickness of 250 micrometers or a Cu-nickel alloy is carried out. Roll pressing down is carried out at 60% of rolling reduction, each part is

pressed down, and homogenizing for 800 degree-Cx 10 minutes is given, and further, at 30% of rolling reduction, roll pressing down is carried out and it is manufactured. Thus, for the obtained compound member 1 for plate-like brazing and soldering, the whole thickness was 420 micrometers and the base material 11 was [50 micrometers and Cu system wax material layer 13 of 300 micrometers and Fe atom diffusion control layer (nickel layer) 12] 70 micrometers. On the other hand, stainless steel sheet steel with a thickness of 200 micrometers was used for the diaphragm. Moreover, brazing-and-soldering conditions are 1100 degree-Cx10min, when Cu system wax material layer is formed with said Cu-Mn-nickel alloy. When it forms with maintenance and said Cu-nickel alloy, it is 1150 degree-Cx10min. It considered as maintenance. In addition, these dimensions are examples and the thing of a proper dimension is used by the specification of a heat exchanger.
Drawing 13 is the sectional view showing the passage structure of the heat exchanger concerning the 2nd operation gestalt. This passage structure is having honeycomb structure, and two or more laminatings of the concave heights material 31 by which the crevice 32 and heights 33 of trapezoidal shape continued by turns, and fabrication was carried out to the wave are carried out in the vertical direction, and it is constituted. ** which attaches the sign of 31-1 and 31-2 to the concave heights material of a certain pair by which contiguity arrangement of the explanation was carried out for convenience up and down. As for the concave heights material 31-1 and 31-2 comrades which adjoin up and down, the brazing and soldering of the external surface (inferior surface of tongue) of the crevice 32 of the upper wave member 31-1 and the external surface (top face) of the heights 33 of the lower concave heights material 31-2 are carried out mutually. On the other hand, between the heights 33 of the upper concave heights material 31-1, and the crevice 32 of the lower concave heights material 31-2, much space sections of 6 square-shape cross section are formed, and it is in it. Let this space section be the medium passage W where gas-passageway G to which high-temperature-corrosion nature gas, such as exhaust gas, flows, and heat exchange media, such as cooling water, flow. In addition, in the example of drawing, gas-passageway G and the medium passage W are arranged by turns at right and left.
As shown in the material of the concave heights material 31 of said heat exchanger at drawing 14 , compound member 31A for concave convex brazing and soldering by which fabrication was carried out concave convex is used for magnitude with the proper composite 1 for brazing and soldering which has the cross-section structure shown in drawing 1 . The amount of [said composite 1 for brazing and soldering and] said division attaches and explains a same sign also to the expedient top of explanation, and compound member 31A for this concave convex brazing and soldering. The clad of the Cu system wax material layer 13 to which compound member 31A for concave convex brazing and soldering consists of pure Cu Fe atom diffusion control layer 12 which becomes both sides of the base material 11 of the shape of sheet metal formed with the SUS304 stainless steel of JIS like the 1st operation gestalt from nickel layer, and on it is carried out by diffused junction.
In order to assemble a heat exchanger using said compound member 31A for concave convex brazing and soldering A laminating is carried out, as inferior lamella section 32of upper compound member 31A for concave convex brazing and soldering A and superior lamella section 33of lower compound member 31A for concave convex brazing and soldering A are piled up and it is shown in drawing 13 . What is necessary is to be more than the melting point of Cu in a vacuum or a reducing gas ambient atmosphere, and just to heat at the proper temperature T1 of under the melting point of nickel. Cu system wax material layer 13 of the compound members 31A and 31A for concave convex brazing and soldering by which opposite

arrangement was carried out up and down, and 13 comrades fuse and unify, and brazing and soldering are carried out by this. Under the present circumstances, corrosion-resistant degradation of the wax material section which it was controlled that Fe atom is spread in a wax material side from the base material 11 of compound member 31A for concave convex brazing and soldering (concave heights material 31), it once fused, and was solidified is prevented in an operation of Fe atom diffusion control layer 12.
Here, presentation change of brazing-and-soldering temperature and wax material is explained. Drawing 15 shows the state diagram of a Cu-nickel binary system alloy, and when heating maintenance is carried out by T1 in drawing, it can control the amount of nickel in wax material by the holding time between N1-N2. Although the corrosion resistance of the wax material section after brazing and soldering improves so that nickel melts into a wax material side from nickel layer to about 20wt%, the thickness of nickel layer decreases. What is necessary is just to form it about 10 micrometers or more preferably about 5 micrometers or more with about dozens of minutes, since the holding time at the time of carrying out brazing and soldering at about 1000-1200 degrees C industrially is a short time comparatively although the thickness of nickel layer which is Fe atom diffusion control layer 12 is strictly determined in consideration of this decrement. Moreover, the wax material section excellent in corrosion resistance can be formed also by short-time brazing and soldering by forming Cu system wax material layer with a Cu-5-10wt%nickel alloy.
The brazing-and-soldering structure of this invention is not interpreted more restrictively than the heat exchanger of this 1st and 2nd operation gestalt. Moreover, it is not restrictively interpreted according to the above-mentioned operation gestalt about a heat exchanger.
For example, the laminating number of stages of the plate member 21 of the 1st operation gestalt and the laminating number of stages of the concave heights material 31 of the 2nd operation gestalt can be freely set up according to a demand. Moreover, it comes out to use the various quality of the materials explained in the composite 1 for brazing and soldering as Fe atom diffusion control layer 11 which constitutes compound member 21for plate-like brazing and soldering A with which manufacture of the heat exchanger of the above-mentioned 1st and 2nd operation gestalt was presented, and compound member 31A for concave convex brazing and soldering, and a Cu system wax material layer 13.
Moreover, what is necessary is it to be good if Fe atom of a base material 11 does not diffuse the thickness of Fe atom diffusion control layer 12 in Cu system wax material side in the case of brazing and soldering, and just to set it as about 10 micrometers or more more preferably about 8 micrometers or more about 5 micrometers or more, although thickness of Fe atom diffusion control layer 12 was set to 50 micrometers with the above-mentioned 1st operation gestalt.
Moreover, with the above-mentioned 1st operation gestalt, although the diaphragm 22 used stainless steel sheet metal, it may use what carried out laminating formation of the Fe atom diffusion control layer by using stainless steel sheet metal as a base material also about the diaphragm, and the thing in which Cu system wax material layer was formed on Fe atom diffusion control layer, still like drawing 1 . By forming Fe atom diffusion control layer, it can prevent carrying out diffusion invasion to the wax material which Fe atom fused from the base material of a diaphragm on the occasion of brazing and soldering, and corrosion-resistant degradation of the brazing-and-soldering section to which the brazing and soldering of the diaphragm were carried out can be controlled further.
Moreover, although the clad of the Cu system wax material layer 13 besides Fe atom diffusion control layer 12 was carried out to the compound members 21A and 31A for brazing and

soldering, Cu system wax material layer 13 is not necessarily required of the above-mentioned 1st and 2nd operation gestalt. In this case, Cu system wax material prepared separately is attached between the compound member for plate-like brazing and soldering, and a diaphragm, or between the members for concave convex brazing and soldering, and should just be made to carry out brazing and soldering.
Moreover, what is necessary is just to carry out laminating formation of Fe atom diffusion control layer 12 and the Cu system wax material layer 13 with the above-mentioned 1st and 2nd operation gestalt, at the side which carries out the brazing and soldering of other members at least, although Fe atom diffusion control layer 12 and Cu system wax material layer 13 were formed in both sides of the compound members 21A and 31A for brazing and soldering. For example, what is necessary is to form Fe atom diffusion control layer 12 grade only in the side which carries out the brazing and soldering of the diaphragm 22 about the compound member for brazing and soldering used as the plate member 21-1 of a lot shown in drawing 12 , and a material of 21-2.
Availability on industry The composite for brazing and soldering of this invention is suitably used as a material of the brazing-and-soldering structures, such as a heat exchanger used under a corrosive ambient atmosphere. Moreover, since the corrosion resistance of the wax material section is excellent, the brazing-and-soldering structure of this invention and a heat exchanger are suitably used for the bottom of high-temperature-corrosion nature ambient atmospheres, such as exhaust gas.
Explanation of a sign 1 Composite for brazing and soldering 11 Base material 12 Fe atom diffusion control layer 13 Cu system wax material layer 21-1, 21-2 Plate member 21A Compound member for plate-like brazing and soldering 22 Diaphragm 31 Concave heights material 31A Compound member for concave convex brazing and soldering

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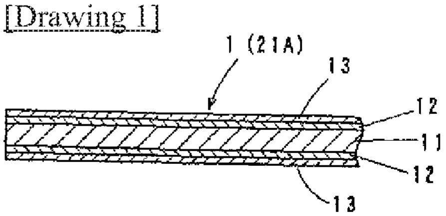
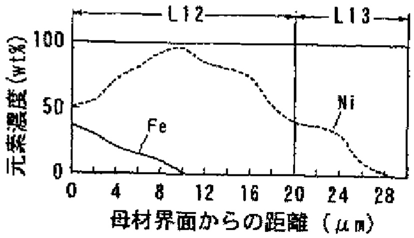
[Translation done.]

DRAWINGS

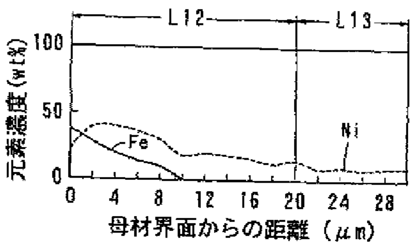
[Drawing 1]



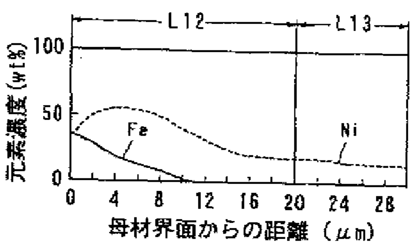
[Drawing 2]



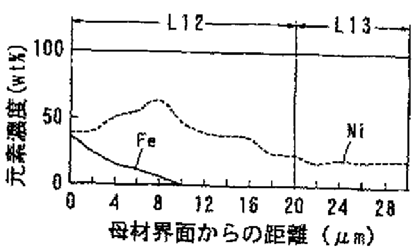
[Drawing 3]



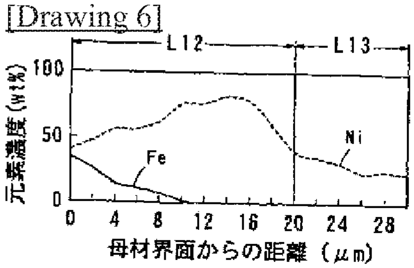
[Drawing 4]



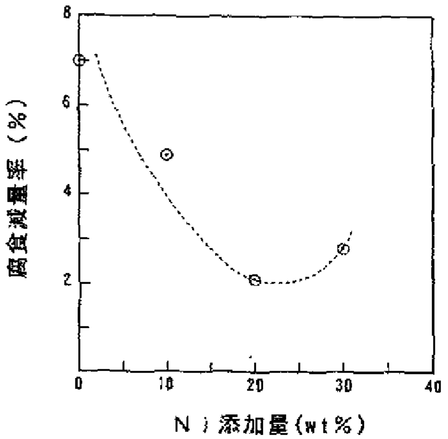
[Drawing 5]



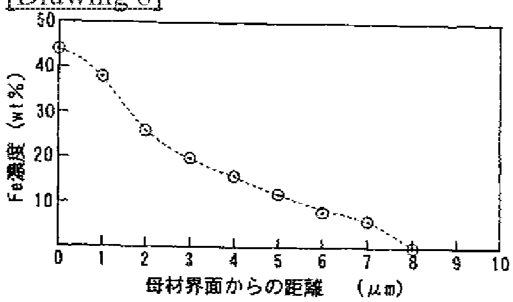
[Drawing 6]



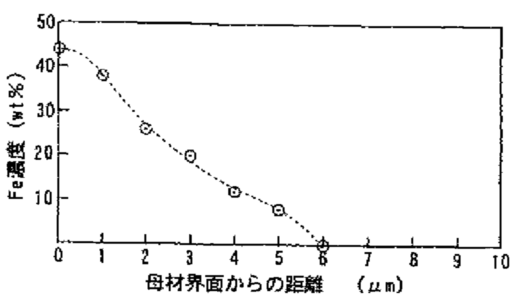
[Drawing 7]



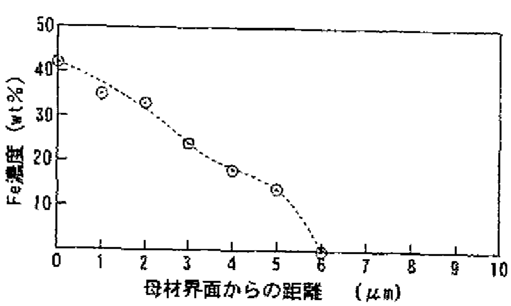
[Drawing 8]



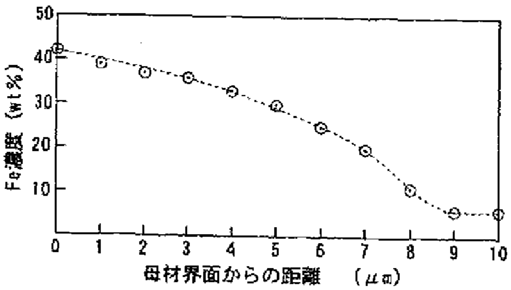
[Drawing 9]



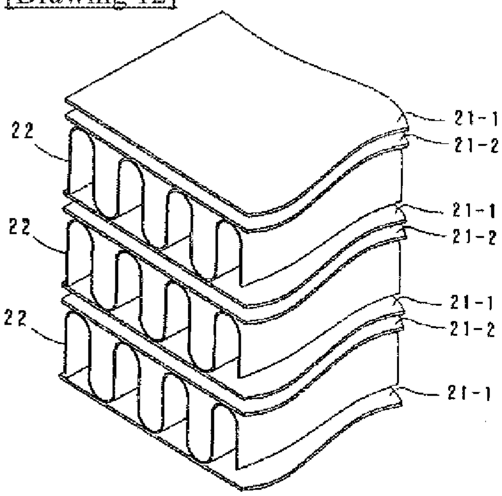
[Drawing 10]



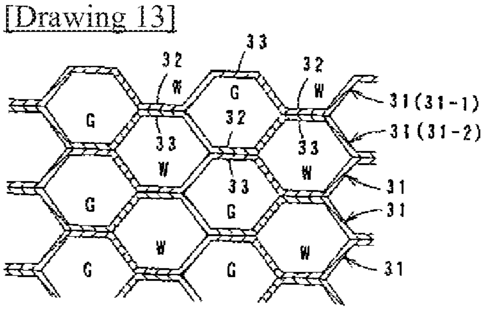
[Drawing 11]



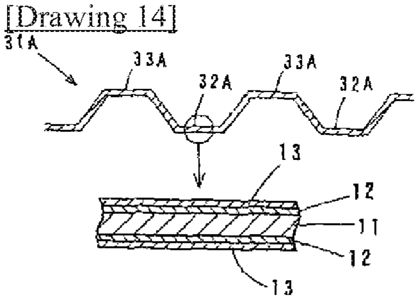
[Drawing 12]



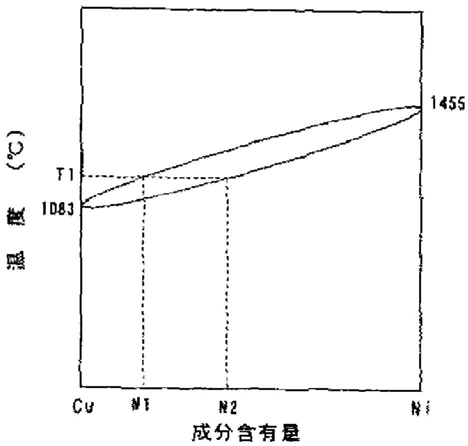
[Drawing 13]



[Drawing 14]



[Drawing 15]



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最終頁に続く

(54)【発明の名称】　ろう接用複合材及びろう接構造物

(57)【特許請求の範囲】
【請求項１】　鉄鋼材により形成された母材と、前記母材の表面に積層形成され、Ｃｕ系ろう材によって接合部材をろう接する際に前記母材からＦｅ原子がろう材側に拡散するのを抑制するＦｅ原子拡散抑制層とを備えた、ろう接用複合材。
【請求項２】　前記母材と前記Ｆｅ原子拡散抑制層とが拡散接合によりクラッドされた、請求の範囲第１項に記載したろう接用複合材。
【請求項３】　鉄鋼材により形成された母材と、前記母材の表面に積層形成され、Ｃｕ系ろう材によって接合部材をろう接する際に前記母材からＦｅ原子がろう材側に拡散するのを抑制するＦｅ原子拡散抑制層と、前記Ｆｅ原子拡散抑制層の上に積層形成されたＣｕ系ろう材層とを備えた、ろう接用複合材。

【請求項４】　前記母材と前記Ｆｅ原子拡散抑制層と前記Ｃｕ系ろう材層とが互いに拡散接合によりクラッドされた、請求の範囲第３項に記載したろう接用複合材。
【請求項５】　前記母材がステンレス鋼材で形成され、前記Ｆｅ原子拡散抑制層がＮｉあるいはＮｉを主成分とするＮｉ合金で形成された、請求の範囲第１～４項のいずれか１項に記載したろう接用複合材。
【請求項６】　前記母材がステンレス鋼材で形成され、前記Ｆｅ原子拡散抑制層がＮｉあるいはＮｉを９０wt%以上含有し、残部Ｃｕを本質的成分としてなるＮｉ－Ｃｕ合金で形成され、前記Ｃｕ系ろう材層がＮｉを２～１５wt%含有し、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成された、請求の範囲第４項に記載したろう接用複合材。
【請求項７】　前記Ｃｕ系ろう材層を形成するＣｕ－Ｎ

ｉ合金はＮｉを５～１０wt%含有し、残部Ｃｕを本質的成分としてなる、請求の範囲第６項に記載したろう接用複合材。

【請求項８】　前記Ｆｅ原子拡散抑制層の厚さが５μｍ以上である、請求の範囲第１～７項のいずれか１項に記載したろう接用複合材。

【請求項９】　第１部材と、この第１部材にＣｕ系ろう材によってろう接された第２部材とを備え、
前記第１部材は鉄鋼材により形成された母材と、前記母材の表面に積層され、前記第１部材と第２部材とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＦｅ原子拡散抑制層とを有する、ろう接構造物。

【請求項１０】　前記母材がステンレス鋼で形成され、前記Ｆｅ原子拡散抑制層はＮｉあるいはＮｉを主成分とするＮｉ合金で形成された、請求の範囲第９項に記載したろう接構造物。

【請求項１１】　対向して配置されたプレート部材と、前記プレート部材の間に形成された空間部を多数の部分空間部に仕切る仕切り部材とを備え、
前記プレート部材と前記仕切り部材とがＣｕ系ろう材によってろう接され、
前記プレート部材はステンレス鋼により形成されたプレート状母材と、前記母材の表面に積層形成され、前記仕切り部材と前記プレート部材とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＮｉあるいはＮｉを主成分とするＮｉ合金からなるＦｅ原子拡散抑制層とを有する、熱交換器。

【請求項１２】　第１凹部と第１凸部とが交互に形成された第１凹凸部材と、前記第１凹凸部材に対向して配置され、第２凹部と第２凸部とが交互に形成された第２凹凸部材とを備え、
前記第１凹凸部材の第１凹部の外面と前記第２凹凸部材の第２凸部の外面とがＣｕ系ろう材によってろう接され、
前記第１凹凸部材および第２凹凸部材は各々ステンレス鋼により形成された母材と、前記母材の表面に積層形成され、前記第１凹部と前記第２凸部とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＮｉあるいはＮｉを主成分とするＮｉ合金からなるＦｅ原子拡散抑制層とを有する、熱交換器。

【請求項１３】　前記Ｃｕ系ろう材はＮｉを５～１０wt%含有し、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成され、前記Ｆｅ原子拡散抑制層はＮｉあるいはＮｉを９０wt%以上含有し、残部Ｃｕを本質的成分としてなるＮｉ－Ｃｕ合金で形成された、請求の範囲第１１項または第１２項に記載した熱交換器。

【発明の詳細な説明】

技術分野

本発明は、ラジエーター、ガスクーラーなどの熱交換器等のろう接構造物およびその素材として使用されるろう接用複合材に関する。

背景技術

近年、国際的に環境問題への関心が高まっており、その一環として自動車の排気ガス低減が強く要求されるようになってきている。自動車の排気ガス浄化対策として、すでに排気ガスを再燃焼させてＣＯ、ＨＣをCO_2、H_2Oにするサーマルリアクターや触媒コンバーターなどの各種の浄化装置が実用化されている。

従来、排ガス浄化装置等において、高温の腐食性ガス雰囲気で用いられる熱交換器は、耐食性に優れたステンレス鋼で形成され、熱交換器の各部材は、１０００℃以上の融点を持つ、耐食性の良好な銅ろうや、特開昭６０－７２６９５号公報に記載されたMn；５～２０%、あるいはさらにＮｉ：１～５%、残部実質的にＣｕからなるＣＵ系ろう材によってろう接される。

最近、排ガス組成の変化などによって熱交換器内の腐食環境が一段と厳しくなってきており、排ガスの凝縮液による腐食などの問題も生じているため、ろう材の耐食性に対してより一層の向上が求められている。このような高腐食環境に曝されるろう材の耐食性への要求は、自動車の排ガス浄化システムだけの問題ではなく、ガスタービンエンジン等の排ガス熱交換器や、高腐食環境に曝される各種ろう接鉄鋼構造物においても求められているところである。

しかしながら、このような耐食性の要求を十分満足するろう材は、未だ市場に供給されていないのが現状である。耐食性が良好といわれるＮｉろうを用いた場合においても、高温環境では問題がないものの、排ガスが結露するような環境下ではやはり腐食が進行する。この理由は必ずしも明らかではないが、ＮｉろうにはＢやＳｉなどの融点低下元素が添加されていることも原因の一つであると推測される。また、耐食性向上元素であるＮｉを比較的多く添加したＣｕ－Ｎｉ合金ろう材を用いても、十分な耐食性が得られない。しかも、Ｎｉ量が多いほど、耐食性が劣化するという現象も認められた。

本発明はかかる課題に鑑みなされたもので、ステンレス鋼材を含む各種鉄鋼材により形成された部材がろう接されたろう接構造物において、ろう材部の耐食性を向上させることができるろう接用材料、および腐食雰囲気に曝されるろう材部における耐食性に優れた熱交換器等のろう接構造物を提供することを目的とするものである。この目的は以下の発明により達成される。

発明の開示

本発明のろう接用材料は、鉄鋼材により形成された母材と、前記母材の表面に積層形成され、Ｃｕ系ろう材によって接合部材をろう接する際に前記母材からＦｅ原子がろう材側に拡散するのを抑制するＦｅ原子拡散抑制層とを備えた、ろう接用複合材である。

この発明によると、母材の表面にはＦｅ原子拡散抑制

層が形成されているので、ろう接の際、母材中のＦｅ原子がろう材側に拡散するには、Ｆｅ原子拡散抑制層をまず拡散移動する必要がある。Ｆｅ原子拡散抑制層におけるＦｅ原子の拡散は固相拡散となるため、Ｆｅ原子の拡散速度は溶融状態のろう材中を拡散するのに比して著しく遅くなる。このため、ごく薄いＦｅ原子拡散抑制層を設けるだけで、Ｆｅ原子がろう材中に拡散するのを防止することができる。その結果、ろう接構造物のろう材部はＣｕ系ろう材が本来有する耐食性を発揮することができるようになり、耐食性が向上する。

この発明において、Ｆｅ原子拡散抑制層の上にＣｕ系ろう材層を形成しておくことができる。また、母材とＦｅ原子拡散抑制層とを、またＦｅ原子拡散抑制層とＣｕ系ろう材層とを拡散接合によりクラッドすることができる。また、に記載したように、前記母材をステンレス鋼材で、前記Ｆｅ原子拡散抑制層をＮｉあるいはＮｉを主成分とするＮｉ合金で形成することができる。また、母材とＦｅ原子拡散抑制層とＣｕ系ろう材層とを拡散接合によりクラッドする場合、母材をステンレス鋼材で、Ｆｅ原子拡散抑制層をＮｉあるいはＮｉを９０wt%以上含有し、残部Ｃｕを本質的成分としてなるＮｉ－Ｃｕ合金で、前記Ｃｕ系ろう材層をＮｉを２～１５wt%、より好ましくは５～１０wt%含有し、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成するのがよい。さらに、前記Ｆｅ原子拡散抑制層の厚さは、５μm以上とするのがよい。

また、本発明のろう接構造物は、第１部材と、この第１部材にＣｕ系ろう材によってろう接された第２部材とを備える。前記第１部材は鉄鋼材により形成された母材と、前記母材の表面に積層され、前記第１部材と第２部材とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＦｅ原子拡散抑制層とを有する。

この発明によると、ろう接の際、第１部材の母材中のＦｅ原子はまずＦｅ原子拡散抑制層を固相拡散しなければならないため、溶融状態のろう材側に拡散侵入することが抑制される。このため、ごく薄いＦｅ原子拡散抑制層を設けるだけで、Ｆｅ原子がろう材中に拡散するのを防止することができる。その結果、ろう接構造物のろう材部はＣｕ系ろう材が本来有する耐食性を発揮することができるようになり、耐食性が向上する。第２部材が鉄鋼材で形成される母材を有する場合には、第１部材と同様、母材の上にＦｅ原子拡散抑制層を形成することが好ましい。これによって、第２部材の母材からＦｅ原子がろう材部へ拡散することも抑制することができ、ろう材部の耐食性をより向上させることができる。

前記ろう接構造物において、前記母材をステンレス鋼で形成し、前記Ｆｅ原子拡散抑制層をＮｉあるいはＮｉを主成分とするＮｉ合金で形成することができる。この場合、母材自体が耐食性に優れ、さらにＦｅ原子拡散抑制層と母材との熱膨張率が近似するようになるため、広範囲の温度下でＦｅ原子拡散抑制層と母材との接合部において熱応力の発生が抑制され、接合部の耐久性を向上させることができる。

また、本発明の熱交換器は、対向して配置されたプレート部材と、前記プレート部材の間に形成された空間部を多数の部分空間部に仕切る仕切り部材とを備える。前記プレート部材と前記仕切り部材とがＣｕ系ろう材によってろう接される。前記プレート部材はステンレス鋼により形成されたプレート状母材と、前記母材の表面に積層形成され、前記仕切り部材と前記プレート部材とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＮｉあるいはＮｉを主成分とするＮｉ合金からなるＦｅ原子拡散抑制層とを有する。

この発明によると、ろう接の際、プレート部材の母材中のＦｅ原子はまずＦｅ原子拡散抑制層を固相拡散しなければならないため、ごく薄いＦｅ原子拡散抑制層を設けるだけで、溶融状態のろう材側に拡散侵入することが防止される。その結果、ろう接構造物である熱交換器のろう材部はろう材が本来有する耐食性を発揮することができ、耐食性が向上する。また、母材自体が耐食性に優れ、さらにＦｅ原子拡散抑制層はＮｉあるいはＮｉを主成分とするＮｉ合金によって形成されるので、母材のステンレス鋼と熱膨張率が近似しているため、広範囲の温度下で熱応力の発生が抑制され、熱交換器の耐久性を向上させることができる。

また、本発明の熱交換器は、第１凹部と第１凸部とが交互に形成された第１凹凸部材と、前記第１凹凸部材に対向して配置され、第２凹部と第２凸部とが交互に形成された第２凹凸部材とを備える。前記第１凹凸部材の第１凹部の外面と前記第２凹凸部材の第２凸部の外面とがＣｕ系ろう材によってろう接される。前記第１凹凸部材および第２凹凸部材は各々ステンレス鋼により形成された母材と、前記母材の表面に積層形成され、前記第１凹部と前記第２凸部とがろう接される際に前記母材からＦｅ原子がろう材部に拡散するのを抑制するＮｉあるいはＮｉを主成分とするＮｉ合金からなるＦｅ原子拡散抑制層とを有する。

この発明によると、ろう接の際、第１凹凸部材および第２凹凸部材の各母材中のＦｅ原子は、まず各部材のＦｅ原子拡散抑制層を固相拡散しなければならないため、各母材の上にごく薄いＦｅ原子拡散抑制層を設けるだけで、溶融状態のろう材側に拡散侵入することが防止される。その結果、ろう接構造物である熱交換器のろう材部はろう材が本来有する耐食性を発揮することができ、耐食性が向上する。また、母材自体が耐食性に優れ、さらにＦｅ原子拡散抑制層はＮｉあるいはＮｉを主成分とするＮｉ合金によって形成されるので、母材のステンレス鋼と熱膨張率が近似しているため、広範囲の温度下で熱応力の発生が抑制され、熱交換器の耐久性を向上させる

ことができる。

前記熱交換器において、前記Ｃｕ系ろう材をＮｉを５～１０wt%含有し、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で、前記Ｆｅ原子拡散抑制層をＮｉあるいはＮｉを９０wt%以上含有し、残部Ｃｕを本質的成分としてなるＮｉ－Ｃｕ合金で形成することで、ろう材部の耐食性をより一層向上させることができる。

図面の簡単な説明

図１は、本発明の実施形態にかかるろう接用複合材の部分断面図である。

図２は、Ｃｕ系ろう材層を純Ｃｕで形成したろう接用複合材を１１００℃で１０min 保持した場合の母材界面からろう材層表面におけるＮｉ濃度およびＦｅ濃度の分布図である。

図３は、Ｃｕ系ろう材層をＣｕ－２wt%Ｎｉ合金で形成したろう接用複合材を１１５０℃で１０min 保持した場合の母材界面からろう材層表面におけるＮｉ濃度およびＦｅ濃度の分布図である。

図４は、Ｃｕ系ろう材層をＣｕ－５wt%Ｎｉ合金で形成したろう接用複合材を１１５０℃で１０min 保持した場合の母材界面からろう材層表面におけるＮｉ濃度およびＦｅ濃度の分布図である。

図５は、Ｃｕ系ろう材層をＣｕ－１０wt%Ｎｉ合金で形成したろう接用複合材を１１５０℃で１０min 保持した場合の母材界面からろう材層表面におけるＮｉ濃度およびＦｅ濃度の分布図である。

図６は、Ｃｕ系ろう材層をＣｕ－２０wt%Ｎｉ合金で形成したろう接用複合材を１２００℃で１０min 保持した場合の母材界面からろう材層表面におけるＮｉ濃度およびＦｅ濃度の分布図である。

図７は、Ｃｕ－Ｎｉ合金ろう材におけるＮｉ含有量と腐食減量率との関係を示す図である。

図８は、実施例にかかるろう接複合材を１１００℃で１０min 保持した場合の母材界面からＦｅ原子拡散抑制層の板厚方向のＦｅ濃度分布図である。

図９は、実施例にかかるろう接複合材を１０５０℃で１０min 保持した場合の母材界面からＦｅ原子拡散抑制層の板厚方向のＦｅ濃度分布図である。

図１０は、実施例にかかるろう接複合材を１０００℃で１０min 保持した場合の母材界面からＦｅ原子拡散抑制層の板厚方向のＦｅ濃度分布図である。

図１１は、Ｆｅ原子拡散抑制層が形成されていない比較例にかかるろう接複合材を１１００℃で１０min 保持した場合の母材界面からろう材層の板厚方向のＦｅ濃度分布図である。

図１２は、第１実施形態にかかる熱交換器の部分斜視図である。

図１３は、第２実施形態にかかる熱交換器の部分断面図である。

図１４は、第２実施形態の熱交換器の製造に使用した凹凸状ろう接用複合部材の部分断面図および部分拡大断面図である。

図１５は、Ｃｕ－Ｎｉ２元合金の状態図である。

発明を実施するための最良の形態

本発明者は、ステンレス鋼等の鉄鋼材で形成された接合部材同士をＣｕ系ろう材によってろう接したろう接構造物において、そのろう材部の耐食性が劣化する原因を究明した。その結果、９００℃を越えるような高温でろう接すると、鉄鋼材からＦｅ原子が溶融したろう材中に拡散侵入し、Ｆｅ原子がろう材部の表面にまで拡散するため、ろう材部の耐食性が接合前のＣｕ系ろう材の本来の耐食性を発揮できず、劣化することを知見した。すなわち、ＦｅはＣｕより腐食されやすく、またＦｅとＣｕとが局部電池を構成するので、ろう材部における耐食性が、ろう接の際に用いたＣｕ系ろう材の本来有する耐食性に比して劣化するようになる。このため、Ｆｅが拡散侵入したろう接後のろう材部が腐食雰囲気に曝されると、腐食されやすくなる。なお、鉄鋼材中の合金元素、例えばステンレス鋼中のＮｉやＣｒもろう接の際にろう材側に拡散するが、ＮｉはＣｕに固溶するため耐食性を損なわず、またＣｒはＦｅに比して拡散速度が遅いため、耐食性を損なうほどには拡散しないものと考えられる。本発明はかかる知見により完成されたものである。

以下、本発明を実施形態に基づいて詳細に説明する。

図１は本発明の実施形態にかかるろう接用複合材１を示しており、プレート状の母材１１の両面にＦｅ原子拡散抑制層１２、１２が積層形成され、その上にＣｕ系ろう材層１３、１３が積層形成されている。

前記母材１１としては、Ｆｅを主成分とする鉄鋼材であればいずれの材質のものでも適用することができる。好適には耐食性の良好な鉄鋼材、例えばステンレス鋼材などで形成するのがよい。

前記Ｆｅ原子拡散抑制層１２としては、Ｆｅを含まず、融点がろう材よりも高く、Ｃｕと固溶する金属、従って腐食の起点になりやすい析出物を生成しない金属で形成することができる。例えば、純Ｎｉ、Ｎｉを主成分（好ましく５０wt%以上）とするＮｉ合金や、Ｃｒ、Ｍｏ、Ｗ、Ｎｂ、Ｔｉ等を用いることができる。前記Ｎｉ合金としてはＮｉ－Ｃｕ合金、Ｎｉ－Ｃｒ合金、Ｎｉ－Ｍｏ合金を例示することができる。塑性加工性を考慮した場合、前記Ｎｉ－Ｃｒ系合金ではＮｉ≧７０wt%、Ｎｉ－Ｍｏ系合金ではＮｉ≧９０wt%以上とすることが好ましい。また、Ｎｉ合金としては前記Ｃｒ、Ｍｏなどの合金元素のほか、合金の基本的性質を損なわず、機械的、化学的特性を向上させる元素が補助的に含有されたものでもよい。なお、Ｆｅ原子拡散抑制層をＷ、Ｍｏ等の高融点金属で形成した場合、これを母材にクラッド法により圧接することは困難であるが、溶射、ＰＶＤ、ＣＶＤにより母材の表面に積層形成することができる。

前記母材１１をステンレス鋼で形成した場合、Ｆｅ原

子拡散抑制層１２は前記純ＮｉあるいはＮｉ合金（両者をまとめてＮｉ基金属ということがある。）で形成することが好ましい。ステンレス鋼とＮｉとの熱膨張率が近接しているため、Ｆｅ原子拡散抑制層１２をＮｉ基金属で形成することにより、広範囲の温度下でＦｅ原子拡散抑制層１２と母材１１との接合部において熱応力の発生を抑制することができ、接合部の耐久性を向上させることができる。因みに、３０～６００℃における熱膨張率は、ＪＩＳ規格のＳＵＳ３０４であるＮｉ－Ｃｒ系ステンレス鋼は１８．３×１０$^{-6}$／Ｋ、ＳＵＳ４３０であるＣｒ系ステンレス鋼は１１．８×１０$^{-6}$／Ｋであり、Ｎｉは１５．４×１０$^{-6}$／Ｋであるのに対して、Ｍｏは５．７×１０$^{-6}$／Ｋ、Ｗは４．６×１０$^{-6}$／Ｋに止まる。なお、排ガス用熱交換器の使用上限温度は、通常、６００℃程度である。

前記Ｃｕ系ろう材層１３としては、純Ｃｕのほか、公知の各種のろう材用Ｃｕ合金、例えばＣｕ－Ｍｎ合金、Ｃｕ－Ｎｉ合金、Ｃｕ－Ｍｎ－Ｎｉ合金を用いることができる。Ｃｕ含有量は、Ｃｕに添加する合金元素によっては１０wt%程度以上あればよい。なお、ろう接の温度は、Ｃｕ系ろう材の融点以上でＦｅ原子拡散抑制層を形成する金属の融点未満の温度とすればよいが、通常、Ｃｕ系ろう材の融点＋２０℃程度の温度とされる。融点が８８０～１１８０℃程度のＣｕ系ろう材を使用することで、ろう接温度を９００～１２００℃程度とすることができ、数分～数１０分間の加熱によりステンレス鋼を含む鉄鋼材の焼鈍とろう接とを同時に行うことができる。

このろう接用複合材１では、Ｆｅ原子拡散抑制層１２の上にＣｕ系ろう材層１３が積層形成されているので、ろう接作業を行う際に、別途準備したろう材をろう接の対象である接合部材の間に付設するといった煩雑な作業が不要となり、ろう接作業性に優れ、生産性を向上させることができる。

前記母材１１へのＦｅ原子拡散抑制層１２の積層形成には、拡散接合によるクラッドのほか、めっき、溶射、ＰＶＤ、ＣＶＤなどの種々の方法が適用可能である。もっとも、母材１１とＦｅ原子拡散抑制層１２とを拡散接合によってクラッドすれば、めっきの場合に問題となるピンホールが生じることもなく、各素材を圧下後、拡散焼鈍することにより両者を容易に一体化することができ、工業的生産性に優れる。また、圧下の際の圧下率を調整するだけでＦｅ原子拡散抑制層１２の厚さも容易に制御することができる。また、Ｆｅ原子拡散抑制層１２の上にＣｕ系ろう材層１３を形成する場合、母材１１、Ｆｅ原子拡散抑制層１２およびＣｕ系ろう材層１３の各素材をおのおの重ね合わせて圧下し、拡散焼鈍することにより、隣接する各部を容易にクラッドすることができる。

前記母材１１とＦｅ原子拡散抑制層１２とＣｕ系ろう材層１３とをクラッドする場合、Ｆｅ原子拡散抑制層１２を純ＮｉあるいはＮｉを９０wt%以上含有し、残部Ｃｕを本質的成分としてなるＮｉ－Ｃｕ合金で形成し、一方Ｃｕ系ろう材層をＮｉを２～１５wt%、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成することが好ましい。Ｎｉが９０wt%以上の高濃度のＦｅ原子拡散抑制層１２と、Ｃｕが９８wt%超の高濃度のＣｕ系ろう材層１３とをクラッドすると、カーケンドル効果によって接合界面付近にガイドが発生し、ろう接用複合材の寸法制度が損なわれるおそれがある。また、Ｃｕ系ろう材層１３のＮｉ量が１５wt%を超えると、ろう材の融点が１２００℃を超えるようになり、ろう接の際の加熱温度が高くなり過ぎる。

さらに、Ｆｅ原子拡散抑制層１２を純ＮｉあるいはＮｉが９０wt%以上のＮｉ－Ｃｕ合金で形成する場合、Ｃｕ系ろう材層はＮｉを５～１０wt%、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成することがより好ましい。Ｃｕ系ろう材層のＮｉ量を５wt%以上とすることで、カーケンドル効果を防止することができ、さらにろう材の融点が１１００℃超となるため、クラッド後のろう接用複合材の焼鈍温度を純Ｃｕの融点（１０８３℃）近傍あるいはそれ以上に上げることができる。焼鈍温度を高めることによって、母材１１としてステンレス鋼を含む鉄鋼材を用いた場合でも母材を十分に軟化させることができ、ろう接用複合材の成形性、加工性を向上させることができるようになる。一方、１０wt%以下とすることで、ろう材の融点が１１８０℃程度以下となり、１２００℃程度以下の温度でのろう接が可能になる。また、Ｃｕ－Ｎｉ合金のＮｉを５～１０wt%とすることで、接合部材をろう接する際、高濃度のＮｉを含有するＦｅ原子拡散抑制層１２から溶融状態にあるろう材中へＮｉが適度に拡散して、ろう接後のろう材部のＮｉ量が１５～２５wt%程度になる。このＣｕ－Ｎｉ合金からなるろう材部は、耐食性に優れるため、排ガス凝縮液に対しても優れた耐食性を発揮することができる。

前記Ｃｕ系ろう材層をＮｉを５～１０wt%、残部Ｃｕを本質的成分としてなるＣｕ－Ｎｉ合金で形成した場合の耐食性向上効果を確かめるため、下記の実施例１～５にかかるろう接用複合材を用いて耐食性調査を行った。

調査に使用した実施例１のろう接用複合材は、ＪＩＳ規格のＳＵＳ３０４ステンレス鋼で形成された厚さ２０００μｍのステンレス薄鋼板（母材素材）に厚さ１００μｍのＮｉ箔（Ｆｅ原子拡散抑制層素材）、さらに厚さ５０μｍのＣｕ系ろう箔（Ｃｕ系ろう層素材）として純Ｃｕ箔を積層して、圧下率６０％でロール圧下して各部を圧接し、１０５０℃×３分の拡散焼鈍を施し、さらに圧下率５０％でロール圧下して製造された。実施例２～５は、実施例１の製造条件に対してＣｕ系ろう箔の材質のみが異なり、実施例１とともに実施例２～５のＣｕ系ろう材箔の材質を下記にまとめて示す。製造された各実施例の複合材は全体の厚さが４３０μｍで、母材は４０

０μｍ、Ｆｅ原子拡散抑制層（Ｎｉ層）は２０μｍ、Ｃｕ系ろう材層は１０μｍであった。製作されたろう接用複合材を外観観察したところ、Ｃｕ系ろう材層を純Ｃｕで形成した実施例１は、表面に局部的な膨出部が所々に観察された。

実施例１：純Ｃｕ

実施例２：Ｃｕ－２wt%Ｎｉ合金

実施例３：Ｃｕ－５wt%Ｎｉ合金

実施例４：Ｃｕ－１０wt%Ｎｉ合金

実施例５：Ｃｕ－２０wt%Ｎｉ合金

以上のようにして製作された５種類の実施例にかかるろう接用複合材は、下記調査No. １～５に示す加熱条件（加熱温度×保持時間）で真空加熱炉にて加熱され、室温まで放冷された後、母材の界面からＦｅ原子拡散抑制層および凝固後のろう材層の厚さ方向における各部位のＮｉ量およびＦｅ量がＥＰＭＡ（electron probe micro analyser）により測定された。その結果を図２～６に示す。図中のＬ１２、Ｌ１３は加熱冷却後のＦｅ原子拡散抑制層、ろう材層を意味する。下記の調査No. における記載内容は、使用したろう接用複合材の種類、加熱条件、測定結果の順に記載されている。

(1) 調査No. １：実施例１、１１００℃×１０min 、図２

(2) 調査No. ２：実施例２、１１５０℃×１０min 、図３

(3) 調査No. ３：実施例３、１１５０℃×１０min 、図４

(4) 調査No. ４：実施例４、１１５０℃×１０min 、図５

(5) 調査No. ５：実施例５、１２００℃×１０min 、図６

Ｃｕ系ろう材層を純Ｃｕで形成した場合を示す図２では、加熱後のろう材層Ｌ１３の表面から５μｍ程度の表層部ではＮｉ量が５wt%程度以下となっていることがわかる。また、ろう材層Ｌ１３におけるＮｉ量は、Ｃｕ系ろう材層をＣｕ－２wt%Ｎｉ合金で形成した場合を示す図３では１０wt%程度が含有され、同層をＣｕ－５wt%Ｎｉ合金で形成した場合を示す図４では少なくとも１５wt%程度が含有され、同層をＣｕ－１０wt%Ｎｉ合金で形成した場合を示す図５では２０wt%程度が含有され、同層をＣｕ－２０wt%Ｎｉ合金で形成した場合を示す図６では３０wt%程度が含有されていることがわかる。一方、Ｆｅ量は、加熱温度が比較的高温であるにもかかわらず、いずれの場合もＦｅ原子拡散抑制層Ｌ１２において母材界面から１０μｍ程度でほぼ０%になり、ろう材層Ｌ１３ではＦｅ原子は認められなかった。

次に、加熱後の実施例複合材におけるろう材層の耐食性を調べるため、純Ｃｕ、Ｃｕ－１０wt%Ｎｉ合金、Ｃｕ－２０wt%Ｎｉ合金、Ｃｕ－３０wt%Ｎｉ合金のろう材を準備し、腐食試験によってその耐食性を調べた。排ガスによる腐食環境は、エンジン停止時に主として問題となる露点腐食環境と、エンジン稼動時に主として問題となる高温腐食環境とを考慮する必要があるが、前者の耐食性が特に問題であるので、腐食試験は前記露点腐食環境に対する条件の下で行われた。前記腐食試験は、排ガス凝縮液を模擬した下記組成の模擬凝縮水を調製し、１００℃の模擬凝縮水中に上記各ろう材を５００ｈｒ浸漬し、浸漬によって減少したろう材の質量（腐食減量）を測定することによって実施された。

・模擬凝縮水組成（ｐＨ４．４）

Cl^-：２０ppm 、SO_4^{2-}：３５０ppm 、NO_3^-：１５０ppm 、NH_4^+：７００ppm 、ギ酸：５００ppm 、酢酸：７００ppm

腐食試験結果を図７に示す。図中の縦軸は、腐食減量を浸漬前のろう材の質量で除した腐食減量率を示している。図７より、Ｎｉ含有量が１５～２５wt%程度のときに耐食性が最良であることがわかる。これより、前記実施例のろう接用複合材では、Ｃｕ系ろう材層として、Ｃｕ－５wt%Ｃｕ合金を用いた実施例３、Ｃｕ－１０wt%Ｎｉ合金を用いた実施例４が特に優れた耐食性を有していることが理解される。

次に、ろう接複合材１における前記Ｆｅ原子拡散抑制層１２の厚さについて詳細に説明する。

ステンレス鋼部材同士をろう接する場合、ろう接の際にステンレス鋼部材の焼鈍も行うことができるように、ろう接温度を１０００～１２００℃程度に設定するのがよい。かかる高温でのろう接の場合でも、Ｆｅ原子拡散抑制層１２の厚さを５μｍ以上、好ましくは８μｍ以上とすることで、母材１１からのＦｅ原子がろう材側に拡散侵入することをかなりの程度阻止することができ、ろう材部の耐食性を向上させることができる。より好ましくは１０μｍ以上とすることで、図２～６から明らかなとおり、１２００℃程度の高温においてもＦｅ原子のろう材側への拡散をほぼ確実に阻止することができる。もちろん、母材がステンレス鋼以外の鉄鋼材で形成した場合も、Ｆｅ原子拡散抑制層の厚さを５μｍ以上、好ましくは８μｍ以上、より好ましくは１０μｍ以上とすることにより、１０００～１２００℃でのろう接により、母材をステンレス鋼材で形成した場合と同様、母材の焼鈍およびＦｅ原子の拡散抑制効果を得ることができる。

ここで、Ｆｅ原子拡散抑制層の厚さとＦｅ原子拡散抑制効果との関係をろう接を模擬した加熱試験に基づいて具体的に説明する。

加熱試験に用いた実施例のろう接用複合材は、ＪＩＳ規格のＳＵＳ３０４ステンレス鋼で形成された厚さ１０５０μｍのステンレス薄鋼板（母材素板）に厚さ２００μｍのＮｉ箔（Ｆｅ原子拡散抑制層素材）、さらに厚さ２５０μｍの１５%Ｍｎ－１０%Ｎｉ－Ｃｕ合金からなるＣｕ系ろう箔（Ｃｕ系ろう層素材）を積層して、圧下率６０%でロール圧下して各部を圧接し、８００℃×１

０分の拡散焼鈍を施し、さらに圧下率３０％でロール圧下して製造された。このようにして製造された複合材は全体の厚さは４２０μｍで、母材は３００μｍ、Ｆｅ原子拡散抑制層（Ｎｉ層）は５０μｍ、Ｃｕ系ろう材層は７０μｍであった。一方、比較例として、Ｆｅ原子拡散抑制層１２を形成することなく、母材に直接Ｃｕ系ろう材層を積層形成したろう接用複合材を準備した。前記比較例の母材の材質、厚さは実施例と同様であり、Ｃｕ系ろう材はＣｕ－３６wt%Ｍｎ－３６．５wt%Ｎｉ合金を使用し、その厚さは実施例と同様の７０μｍとした。

実施例および比較例のろう接用複合材は、下記調査No. １１～１４に示す加熱条件（加熱温度×保持時間）で真空加熱炉にて加熱され、室温まで放冷された後、母材の界面からＦｅ原子拡散抑制層（実施例の場合）またはろう材層（比較例の場合）の厚さ方向における各部位のＦｅ量がＥＰＭＡにより測定された。その結果を図８～１１に示す。下記の調査No. における記載内容は、使用した複合材の種類、加熱条件、測定結果の順に記載されている。

(1) 調査No. １１：実施例、１１００℃×１０min 、図８

(2) 調査No. １２：実施例、１０５０℃×１０min 、図９

(3) 調査No. １３：実施例、１０００℃×１０min 、図１０

(4) 調査No. １４：比較例、１１００℃×１０min 、図１１

図１１より、比較例では母材界面から９μｍまでＦｅ濃度が４２wt%から６wt%まで漸減し、その後ろう材層の表面まで同濃度を示した。これに対して、実施例では、母材界面ではＦｅ濃度が４２～４４％であったが、Ｎｉ層内において界面から６μｍ（図９、図１０の場合）あるいは８μｍ（図８の場合）でＦｅ濃度が０％になった。これより、Ｆｅ原子拡散抑制層１２を５μｍ程度設けるだけで、ろう材層に拡散侵入するＦｅ原子は大幅に減少することがわかる。また、Ｆｅ原子拡散抑制層１３を８μｍ以上積層形成することで、加熱温度が１１００℃程度以下では、母材からＣｕ系ろう材層へのＦｅ原子の拡散侵入を阻止し得ることがわかる。従って、実施形態のろう接用複合材１、またこれを用いてろう接により組み立てたろう接構造物では、ごく薄いＦｅ原子拡散抑制層１２を母材１１の上に積層形成するだけで、母材１１中のＦｅ原子のろう材側への拡散侵入を大幅に減少させることができ、Ｃｕ系ろう材の本来の耐食性が発揮されることがわかる。

以上、本発明のろう接用複合材を実施形態により説明したが、本発明はこれによって限定的に解釈されるものではない。

例えば、上記実施形態では、母材１１の両側にＦｅ原子拡散抑制層１２およびＣｕ系ろう材層１３を積層形成したが、接合部材がろう接される母材の片面側にのみこれらを積層してもよい。

また、上記実施形態では、Ｆｅ原子拡散抑制層１２のほか、Ｃｕ系ろう材層１３をクラッドしたが、Ｃｕ系ろう材層１３は必ずしも必要ではない。この場合、別途準備したＣｕ系ろう材をろう接用複合材と接合部材との間に付設して、ろう接すればよい。

次に、上記実施形態にかかるろう接用複合材１を素材として用いたろう接構造物の実施形態について説明する。

図１２は第１実施形態にかかる熱交換器の流路構造を示す斜視図であり、対向して配置された一組のプレート部材２１－１，２１－２が所定の間隔を隔てて複数組平行に配置され、互いに隣接する二組のプレート部材において、図例では上側組の下側のプレート部材２１－２と、このプレート部材２１－２に対向して配置された下側組の上側のプレート部材２１－１との間に、断面が波形に屈曲形成された蛇腹状の仕切り部材（フィンともいう。）２２が介設されている。前記一組のプレート部材２１－１，２１－２の間の空間部が冷却水等の熱交換媒体が流れる媒体流路とされる。一方、上側組の下側のプレート部材２２－２と下側組の上側のプレート部材２１－１との間で、前記仕切り部材２２により仕切られた多数の部分空間部が排ガス等の高温腐食性ガスが流れるガス流路とされる。なお、一組のプレート部材２１－１，２１－２について、両者を区別しない場合、プレート部材の符号として２１を用いて説明する場合がある。

各仕切り部材２２は、波形凸部の最上部とこの仕切り部材２２を挟持する上側のプレート部材２１－２の下面とがＣｕ系ろう材によってろう接され、また波形凹部の最下部と仕切り部材２２を挟持する下側のプレート部材２１－１の上面とが同様にＣｕ系ろう材によってろう接されている。

前記熱交換器のプレート部材２１の素材には、図１に示す構造を有するろう接用複合材１を適宜の大きさに加工したプレート状ろう接用複合部材２１Ａが用いられる。説明の便宜上、このプレート状ろう接用複合部材２１Ａについても図１を参照して説明する。プレート状ろう接用複合部材２１Ａは、耐食耐酸性に選れたオーステナイト系ステンレス鋼（ＪＩＳ規格のＳＵＳ３０４ステンレス鋼）で形成された薄板状の母材１１の両面に、Ｎｉ層からなるＦｅ原子拡散抑制層１２、およびその上にＣｕ－１５wt%Ｍｎ－１０wt%Ｎｉ合金、あるいはＣｕ－８wt%Ｎｉ合金からなるＣｕ系ろう材層１３が拡散接合によりクラッドされたものである。一方、前記仕切り部材２２は、前記ステンレス鋼からなる薄板を波形に加工したものである。

前記プレート状ろう接用複合部材２１Ａおよび仕切り部材２２を用いて、熱交換器を組み立てるには、仕切り部材２２とプレート状ろう接用複合部材２１Ａとを交互

に重ね合わせて図１２のように積層して保形し、真空中あるいは還元ガス雰囲気中でＦｅ原子拡散抑制層１２の融点未満でＣｕ系ろう材層１３の融点以上の温度、好ましくは１１００～１２００℃で数分～数１０分間加熱する。これによって、プレート状ろう接用複合部材２１ＡのＣｕ系ろう材層１３が溶融し、母材１１にＦｅ原子拡散抑制層１２を介して仕切り部材２２がろう接される。

ろう接の際にＣｕ系ろう材層１３が一旦溶融して凝固したろう材部は、ろう接の際に母材１１からＦｅ原子が溶融したＣｕ系ろう材中に拡散混入することがＦｅ原子拡散抑制層１２によって抑制されるので、Ｆｅ原子の拡散に起因した腐食性の劣化が防止され、耐食性に優れる。特に、Ｃｕ系ろう材層１３を前記Ｃｕ－Ｎｉ合金で形成した場合は、ろう接の際に、Ｎｉ層から適量のＮｉがろう材部に拡散混入するため、ろう材部の耐食性は非常に優れたものとなる。

実際に熱交換器の製造に用いた前記プレート状ろう接用複合部材２１Ａは、厚さ１０５０μｍのステンレス薄鋼板（母材素板）に厚さ２００μｍのＮｉ箔（Ｆｅ原子拡散抑制層素材）、さらに厚さ２５０μｍのＣｕ－Ｍｎ－Ｎｉ合金、あるいはＣｕ－Ｎｉ合金からなるＣｕ系ろう箔（Ｃｕ系ろう層素材）を積層して、圧下率６０％でロール圧下して各部を圧下し、８００℃×１０分の拡散焼鈍を施し、さらに圧下率３０％でロール圧下して製造されたものである。このようにして得られたプレート状ろう接用複合部材１は全体の厚さは４２０μｍで、母材１１は３００μｍ、Ｆｅ原子拡散抑制層（Ｎｉ層）１２は５０μｍ、Ｃｕ系ろう材層１３は７０μｍであった。一方、仕切り部材は、厚さ２００μｍのステンレス薄鋼板を用いた。また、ろう接条件はＣｕ系ろう材層を前記Ｃｕ－Ｍｎ－Ｎｉ合金で形成した場合には１１００℃×１０min 保持、前記Ｃｕ－Ｎｉ合金で形成した場合には１１５０℃×１０min 保持とした。なお、これらの寸法は一例であり、熱交換器の仕様により適宜の寸法のものが使用される。

図１３は第２実施形態にかかる熱交換器の流路構造を示す断面図である。この流路構造はハニカム構造をしており、台形状の凹部３２と凸部３３とが交互に連続して波形に成形加工された凹凸部材３１が上下方向に複数積層されて構成されている。説明の便宜上、上下に隣接配置されたある一対の凹凸部材に対して３１－１，３１－２の符号を付する。上下に隣接する凹凸部材３１－１、３１－２同士は上側の波形部材３１－１の凹部３２の外面（下面）と、下側の凹凸部材３１－２の凸部３３の外面（上面）とが互いにろう接されている。一方、上側の凹凸部材３１－１の凸部３３と下側の凹凸部材３１－２の凹部３２との間には６角形断面の空間部が多数形成されいる。この空間部が排ガス等の高温腐食性ガスが流れるガス流路Ｇと、冷却水等の熱交換媒体が流れる媒体流路Ｗとされる。なお、図例ではガス流路Ｇと媒体流路Ｗとは左右に交互に配置されている。

前記熱交換器の凹凸部材３１の素材には、図１４に示すように、図１に示す断面構造を有するろう接用複合材１が適宜の大きさに凹凸状に成形加工された、凹凸状ろう接用複合部材３１Ａが用いられる。説明の便宜上、この凹凸状ろう接用複合部材３１Ａに対しても前記ろう接用複合材１と同部分は同符号を付して説明する。凹凸状ろう接用複合部材３１Ａは、第１実施形態と同様、ＪＩＳ規格のＳＵＳ３０４ステンレス鋼で形成された薄板状の母材１１の両面に、Ｎｉ層からなるＦｅ原子拡散抑制層１２、およびその上に純ＣｕからなるＣｕ系ろう材層１３が拡散接合によりクラッドされたものである。

前記凹凸状ろう接用複合部材３１Ａを用いて、熱交換器を組み立てるには、上側の凹凸状ろう接用複合部材３１Ａの下板部３２Ａと、下側の凹凸状ろう接用複合部材３１Ａの上板部３３Ａとを重ね合わせて図１３に示すように積層し、真空中あるいは還元ガス雰囲気中でＣｕの融点以上でかつＮｉの融点未満の適宜の温度Ｔ１で加熱すればよい。これによって、上下に対向配置された凹凸状ろう接用複合部材３１Ａ，３１ＡのＣｕ系ろう材層１３，１３同士が溶融し一体化してろう接される。この際、Ｆｅ原子拡散抑制層１２の作用で、凹凸状ろう接用複合部材３１Ａ（凹凸部材３１）の母材１１からＦｅ原子がろう材側に拡散することが抑制され、一旦溶融して凝固したろう材部の耐食性劣化が防止される。

ここで、ろう接温度とろう材の組成変化について説明する。図１５はＣｕ－Ｎｉ２元合金の状態図を示しており、図中のＴ１で加熱保持した場合、保持時間によってろう材中のＮｉ量をＮ１～Ｎ２の間に制御することができる。Ｎｉ層からＮｉが２０wt%程度までろう材側に溶け込むほど、ろう接後のろう材部の耐食性は向上するが、Ｎｉ層の厚さは減少していく。Ｆｅ原子拡散抑制層１２であるＮｉ層の厚さは、厳密にはこの減少量を考慮して決定されるが、工業的に１０００～１２００℃程度でろう接する際の保持時間は数十分程度と比較的短時間であるので、５μm程度以上、好ましくは１０μm程度以上形成すればよい。また、Ｃｕ系ろう材層をＣｕ－５～１０wt%Ｎｉ合金で形成することにより、短時間のろう接によっても、耐食性に優れたろう材部を形成することができる。

本発明のろう接構造物はかかる第１、第２実施形態の熱交換器より限定的に解釈されるものではない。また、熱交換器についても上記実施形態によって限定的に解釈されるものではない。

例えば、第１実施形態のプレート部材２１の積層段数、第２実施形態の凹凸部材３１の積層段数は、要求に応じて自由に設定することができる。また、上記第１、第２実施形態の熱交換器の製造に供されたプレート状ろう接用複合部材２１Ａ、凹凸状ろう接用複合部材３１Ａを構成するＦｅ原子拡散抑制層１１、Ｃｕ系ろう材層１

３としては、ろう接用複合材１において説明した種々の材質を用いることがでる。

また、上記第１実施形態ではＦｅ原子拡散抑制層１２の厚さを５０μｍとしたが、Ｆｅ原子拡散抑制層１２の厚さは、ろう接の際に母材１１のＦｅ原子がＣｕ系ろう材側に拡散しなければよく、５μｍ程度以上、好ましくは８μｍ程度以上、より好ましくは１０μｍ程度以上に設定すればよい。

また、上記第１実施形態では、仕切り部材２２はステンレス鋼薄板を用いたが、仕切り部材についてもステンレス鋼薄板を母材としてＦｅ原子拡散抑制層を積層形成したもの、さらには図１と同様に、Ｆｅ原子拡散抑制層の上にＣｕ系ろう材層を形成したものを用いてもよい。Ｆｅ原子拡散抑制層を形成することで、ろう接の際に、仕切り部材の母材からＦｅ原子が溶融したろう材に拡散侵入するのを防止することができ、仕切り部材がろう接されたろう接部の耐食性劣化をより一層抑制することができる。

また、上記第１、第２実施形態では、ろう接用複合部材２１Ａ、３１ＡにはＦｅ原子拡散抑制層１２のほか、Ｃｕ系ろう材層１３をクラッドしたが、Ｃｕ系ろう材層１３は必ずしも必要ではない。この場合、別途準備したＣｕ系ろう材をプレート状ろう接用複合部材と仕切り部材との間、あるいは凹凸状ろう接用部材の間に付設して、ろう接するようにすればよい。

また、上記第１、第２実施形態では、ろう接用複合部材２１Ａ、３１Ａの両面にＦｅ原子拡散抑制層１２およびＣｕ系ろう材層１３を形成したが、少なくとも他の部材をろう接する側にＦｅ原子拡散抑制層１２およびＣｕ系ろう材層１３を積層形成すればよい。例えば、図１２に示した一組のプレート部材２１－１，２１－２の素材として用いるろう接用複合部材については、仕切り部材２２をろう接する側にのみＦｅ原子拡散抑制層１２等を形成すればよい。

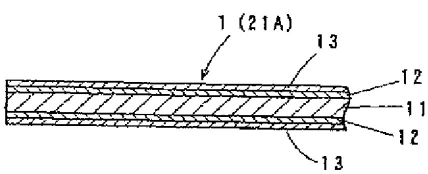
産業上の利用可能性

本発明のろう接用複合材は、腐食性雰囲気下で使用される熱交換器等のろう接構造物の素材として好適に利用される。また、本発明のろう接構造物、熱交換器は、ろう材部の耐食性が優れるので、排ガス等の高温腐食性雰囲気下において好適に利用される。

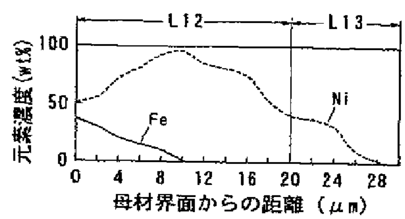
符号の説明

１　ろう接用複合材
１１　母材
１２　Ｆｅ原子拡散抑制層
１３　Ｃｕ系ろう材層
２１－１，２１－２　プレート部材
２１Ａ　プレート状ろう接用複合部材
２２　仕切り部材
３１　凹凸部材
３１Ａ　凹凸状ろう接用複合部材

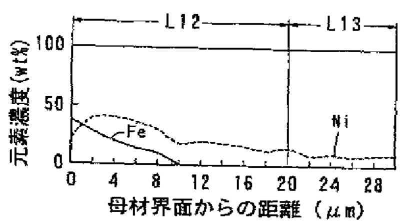
【図１】



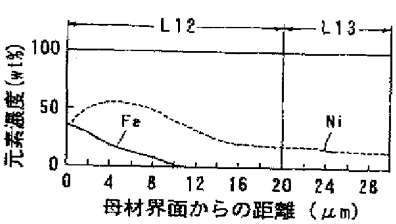
【図２】



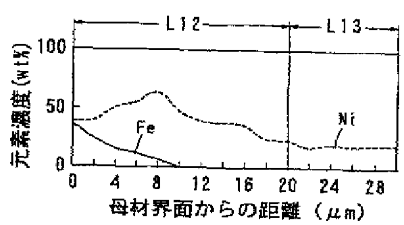
【図３】



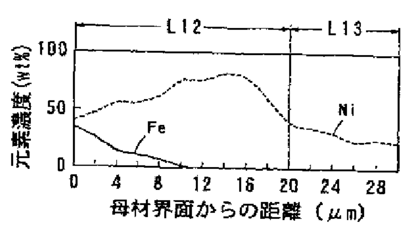
【図４】



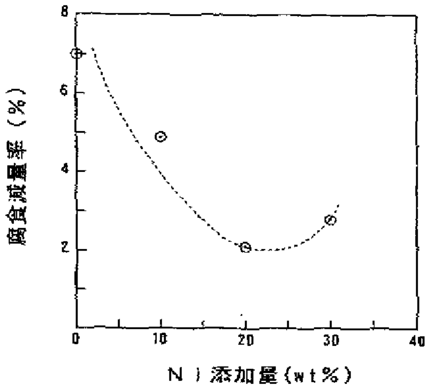
【図５】



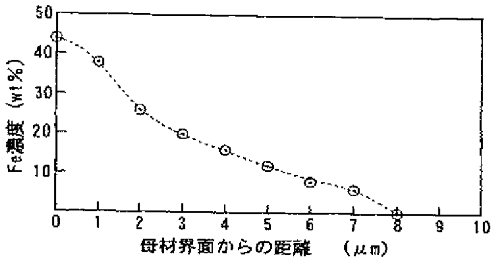
【図６】



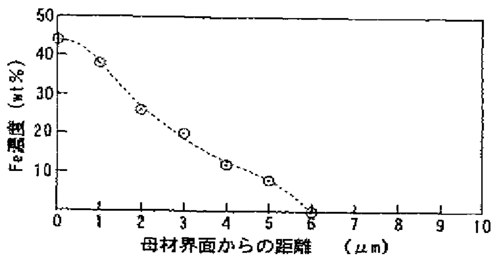
【図７】



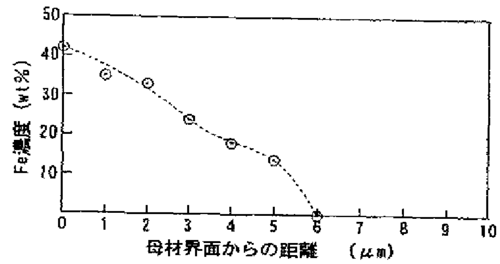
【図８】



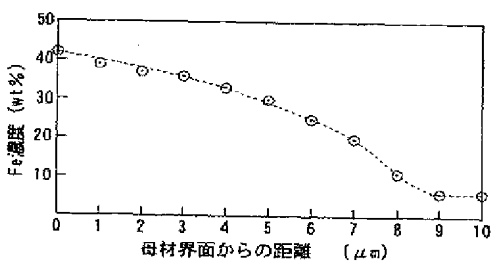
【図９】



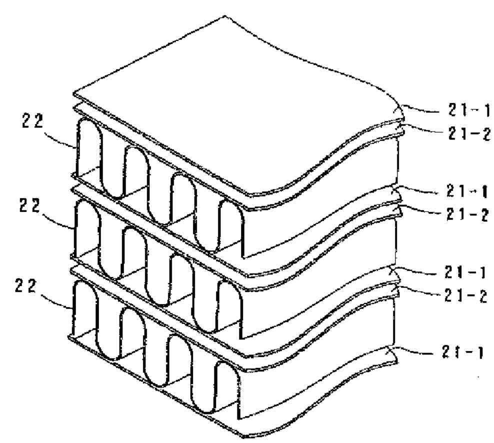
【図１０】



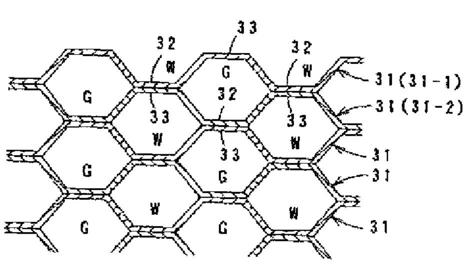
【図１１】



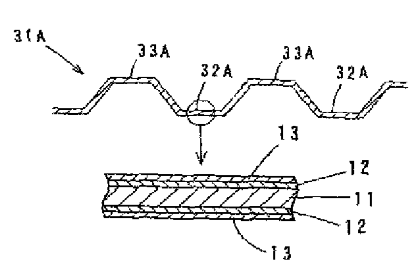
【図１２】



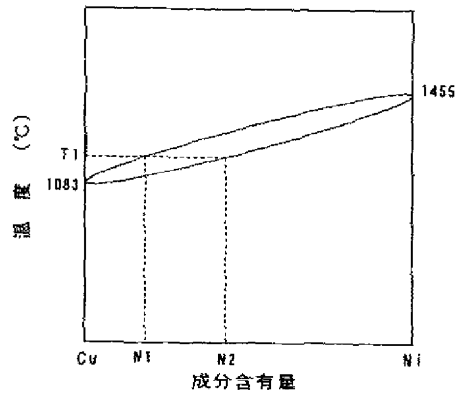
【図１３】



【図１４】



【図１５】



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